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Optical Emission Spectroscopy on Ar/N_2 and $Ar/N_2/C_2H_2$ Expanding Thermal Plasmas

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1. Introduction

This work has been carried out in connection with the possibilities to deposit carbon nitride materials by Expansion Thermal Plasma Assisted Chemical Vapour Deposition (ETP-A-CVD). With the same technique high deposition rates and good quality a-Si:H and a-C:H materials have been obtained [1]. A study of the intensity of atomic lines and molecular bands in a Ar/N_2 and $Ar/N_2/C_2H_2$ expanding thermal plasma has been performed. In the case of the $Ar/N_2/C_2H_2$ mixture rotational and vibrational temperatures were obtained by comparing computer simulated spectra of the CN($B^2\Sigma-X^2\Sigma$, $\Delta v=0$) spectral system bands with the experimental spectra. Details on this computer procedure are given in [2]. The CN ground state density is determined by taking into account the self-absorption of the CN bands.

2. Experimental

The experimental set-up has been described in detail elsewhere [1]. It consists mainly of an arc plasma generated in a flowing gas between three cathodes and a nozzle and stabilised at wall by a cascade of cooled plates. The power injected in the arc can be varied in the range 0.6-5 kW. Gas fluxes up to a few hundred of sccs can be handled in the arc channel. The plasma expands in a vacuumed vessel (diameter 0.4 m, length 1.2 m). Additional gases can be added to the plasma directly in the main flow before the discharge, or in the middle arc channel, or injected some centimetres downstream the nozzle.The spectra have been recorded in the spectral range 350-650 nm by a spectral system consisting of a photomultiplier (Hamamatsu R 268) and a monochromator (Jobin Yvon THR 1000) working in the photon counting mode.

The conditions under which the experiments have been performed are: arc current 75 A, arc pressure 0.3-0.5 bar, background pressure 0.25 mbar, with two mixtures of gases:

a) Ar/ N_2 at fluxes of 95/5 sccs with addition of N_2 in the main flow.

b) $Ar/N_2/C_2H_2$ at fluxes 95/5/2 sccs, with nitrogen added in the main flow and C_2H_2 added in expansion through an injection ring.

The spectra have been recorded in expansion at two positions along the flowing axis:

1) In the mixing zone, at 7 cm from the arc nozzle, 2 centimetres downstream the injection point,

2) In the deposition zone at 62 centimetres from the arc nozzle.

3. Results

3.1 Ar/N2 plasma

a) The addition of nitrogen in the main gas flow produces a strong quenching of the plasma emission as comparing to the pure argon plasma. The spectra recorded near the nozzle (Fig 1a) are dominated by Ar neutral lines. The molecular nitrogen emission is present as well, the N_2^+ FNS spectral system and N_2 SPS spectral system bands having almost the same magnitude; however their intensity is only a few percent of the intensity of Ar lines.

b) For the same plasma settings, the spectrum recorded in the deposition region (Fig. 1b) is dominated by the molecular bands of the ionic molecular nitrogen (FNS); the SPS bands of N_2 are still present but in much lower measure. The Ar lines are hardly observed.

3.2 $Ar/N_2/C_2H_2$ plasma

a) In this case for the spectra recorded in the mixing zone the bands spectrum is much stronger than the line spectrum (Fig 2a). The CH($A^2\Delta$-$X^2\Pi$) and CH($B^2\Delta$-$X^2\Pi$, $\Delta v=0$ with maximum at 413.0 and 388.6 nm) bands and CN($B^2\Sigma$-$X^2\Sigma$, $\Delta v=0$ with maximum at 388.3 nm) bands are the most intense. There is also evidence for the radiation of C_2(A-X, $\Delta v=2$, transitions (2,0) at 438.2 nm, (3,1) at 437.1 nm and (4,2) at 436.5 nm) Swan system which appear in this spectral region superposed over the CH(A-X) bands. The nitrogen SPS and FNS bands have disappeared from the spectrum. The obtained values of rotational and vibrational temperatures and of the CN ground state density have been: Trot=(5690 +/- 200) K , Tvib=(9200 +/- 400) K, [CN(X)]= (1.7 +/- 0.1)x10^{19} m^{-3} .

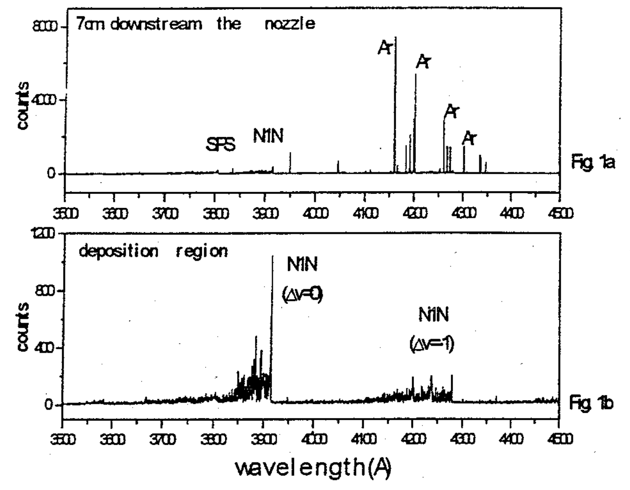

Fig. 1. *a) The spectrum of Ar/N_2 plasma recorded at 7 cm downstream the arc nozzle*
b) The spectrum of Ar/N_2 plasma recorded at 62 cm downstream the nozzle

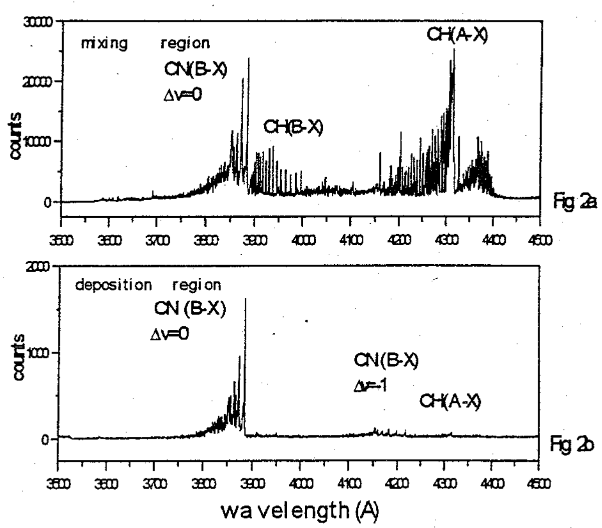

Fig. 2. *a) The spectrum of $Ar/N_2/C_2H_2$ plasma recorded at 7 cm downstream the arc nozzle*
b)The spectrum of $Ar/N_2/C_2H_2$ plasma recorded at 62 cm from the nozzle

b) In the deposition zone the spectrum (Fig. 2b) contains only molecular bands. The main characteristic is that the CN bands are dominating over CH bands which are very weak. The FNS bands are not present anymore. The obtained values of rotational and vibrational temperatures and of the CN ground state density have been: (T_{rot}=6710 +/- 200) K ,T_{vibr}=(6780 +/- 200) K, [CN(X)]= (4.8 +/- 0.2)x10^{18} m^{-3}.

4. Discussion

The observation of the atomic lines dissapearing after injection of C_2H_2 into Ar/N_2 plasma and the molecular bands being very strong indicates that the energy is transferred from the atomic excited species and ions to the molecules. The general behaviour that along the plasma flow axis the lines are disappearing faster than the bands is showing that this process of transfer of energy is also active out of the mixing zone. An explanation of this behaviour could be related to the process of charge transfer to molecular species followed in the case of the $Ar/N_2/C_2H_2$ mixture by a dissociation of the molecule and formation of CH and CN radicals.

A very interesting feature is the behaviour of CN and CH bands along the plasma flow. The spectra show that in the mixing zone both radicals are produced and excited and that only the CN radical survive in the late expansion. This could be related to a higher rate of deposition of the CH radical at the walls or to a higher diffusion of this radical away from the expansion axis towards the walls.
The lower value of the rotational temperature in the mixing zone compared to the deposition zone could be related to the plasma cooling due to the C_2H_2 injection. Along the plasma flow a tendency to equilibration of rotational and vibrational temperatures is noted. However these temperature values are unexpectedly high showing the non-equilibrium character of this plasma . The values of roto-vibrational temperatures in a $Ar/N_2/C_2H_2$ plasma are about twice of those obtained in a Ar/C_2H_2 plasma [2]. The disappearance of emission of FNS bands indicates the importance of the ionic molecular nitrogen in the energy transfer and excitation.

5. Conclusions

In Ar/N_2 and $Ar/N_2/C_2H_2$ expanding thermal plasmas the transfer of energy is from the atomic species towards the molecular species both in the mixing zone and along the expansion. The CN radical is produced in large quantities in the $Ar/N_2/C_2H_2$ expanding thermal plasma. Due to the importance of CN radical in the carbon-nitride deposition it results that Expansion Thermal Plasma Assisted Chemical Vapour Deposition technique is appropriate for this purpose.

6. References

[1] M.C.M. van de Sanden, R.J. Severens, J.W.A.M. Gielen , R.M.J. Pfaffen and D.C. Schram, Plasma Sources Sci. Technol. 5 (1996) 268

[2] E.Aldea, G.Dinescu, J.W.A.M. Gielen, M.C.M van de Sanden , D.C. Schram, ESCAMPIG **B** (1996) 239