Thermal plasma source of hydrogen atoms and ions

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THERMAL PLASMA SOURCE OF HYDROGEN ATOMS AND IONS

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Résumé - Un arc cascade est utilisé comme source d'hydrogène et d'argon. Le plasma est réalisé entre 0,1 et 1 bar et expansé dans une chambre à pression réduite. Les mesures sont effectuées à l'aide d'une double sonde de Langmuir et d'un spectromètre de masse. Les résultats des mesures sont discutés. Les phénomènes moléculaires, tels que les échanges de charge et les recombinaisons dissociatives, ont été définis comme des processus importants.

Abstract - A cascade arc is used as a source for a hydrogen/argon particle beam. The plasma is produced at thermal plasma conditions in the pressure range of 0.1 to 1 bar. It is expanded with a high velocity into a vacuum chamber. Measurements with a Langmuir double probe and with a mass spectrometer are performed. The resulting parameters of the plasma and the extracted ions are discussed. Molecular processes as charge exchange and dissociative recombination appear to be important.

1 - Introduction

With a cascade arc a thermal plasma is produced. By allowing this plasma to expand into a vacuum chamber, a high velocity jet is obtained. This configuration combines an efficient production of reactive particles (radicals, ions) with a large, directed particle flux. The flowing cascade arc has been studied for argon plasmas in relation to carbon deposition /1/. Applications are found in amorphous and crystalline carbon deposition /1,2/, and more recently also in silicon deposition /3/. Hydrogen sources can be used for e.g. proton production, plasma neutralizers /4/ and for production of atomic hydrogen. On a full hydrogen flowing cascade arc so far no experimental experience exists. In the context of plasma neutralization of fast D^- -beams a numerical model has been developed /4/.
In this work we present first experimental results for T_e and n_e on the expanding beam of a hydrogen-argon plasma. Some discussion on the dominant atomic and molecular processes will also be given.

2 - Experimental setup

The apparatus basically consists of a cascade arc and an expansion chamber (fig. 1). The cascade arc consists of a cathode head, a stack of 12 insulated copper plates with a central bore and an anode plate. The central bore is in the first four plates 2 mm, then four plates with a 3 mm bore and finally four with a 4 mm bore, so the arc channel is diverging. At the cathode side argon gas is injected, hydrogen can be added halfway downstream the arc channel. Through the anode plate (bore: 4mm) the plasma is allowed to expand freely into vacuum. Typical operation conditions are a discharge current of 50 A, an argon flow of 2.5 slm and a hydrogen flow of 0.5 slm. The pressure in

the channel is in the range of 0.1-1 bar. The vacuum chamber is a cylindrical vessel with a length of 0.4m and a diameter of 0.4m. A series of two roots blowers and a roughing pump enables a pressure range down to 0.1 Torr at an argon flow rate of 2.5 slm. For diagnostics on the expanding plasma, about 7 cm from the anode plate a Langmuir double probe is mounted. It consists of two tungsten wires, 50 μm diameter, with a 6 mm not insulated tip.

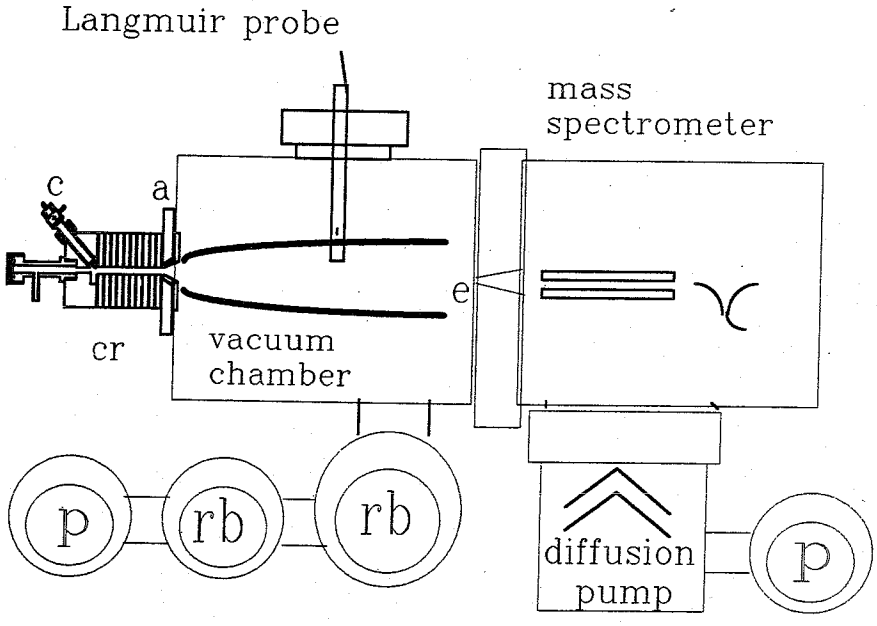
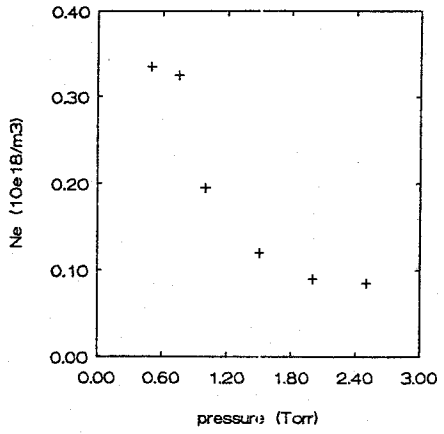


Fig. 1 The apparatus; cr = cascade arc, a = anode, c = cathode, rb = roots blower, p = roughing pump, e = extraction hole.

At the tip, the wires have a distance of approximately 1 mm. The Debye length in the plasma is about 10 μm at typical plasma parameters $n_e = 10^{18}$ m^{-3} and $T_e = 0.5$ eV, so the distance between the wires is about hundred Debye lengths and small compared to temperature and density gradient lengths. Probe measurements give data on electron density and electron temperature in the expansion.
With a mass spectrometer the various positive ion fluxes in the plasma are studied. Particles are extracted at the end of the vessel through a 0.1 mm pinhole in the backwall. The information gained by these measurements gives insight on the occurrence of species and on the fluxes.

3 - Probe measurements

The probe measurements were done at a position on the plasma axis 7 cm from the anode plate. Results are given on the influence of the pressure and of the gas ratio H_2/Ar on n_e and T_e. According to fig. 2a the electron density decreases with increasing pressure above 0.4 Torr. If no recombination processes would be considered, one would expect an increase in density. Such an increase would be the consequence of a narrowing plasma beam, due to a decrease of the ambipolar diffusion coefficient. That a decrease is observed instead, implies that recombination is effective and has a gas pressure dependence. The electron temperature (fig. 2b) also goes down with increasing pressure, although not as fast as the electron density. This is probably due to a larger heat loss of the electrons to vibrational and rotational excitation of molecules.



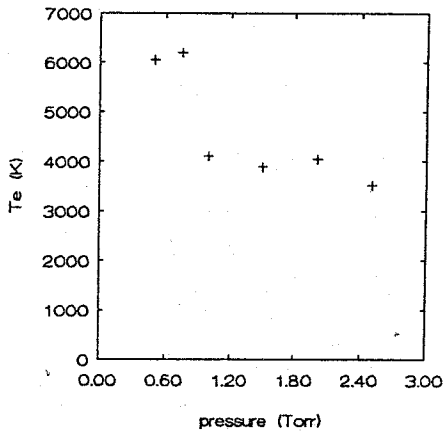
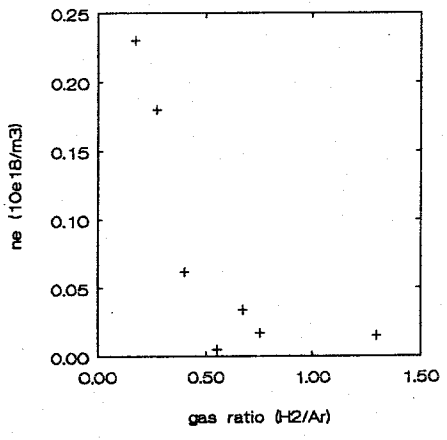


Fig. 2a n_e dependence on pressure
The gas flow is 2.5 slm Ar, 0.5 slm H_2; I_{arc} = 75 A

2b T_e dependence on pressure



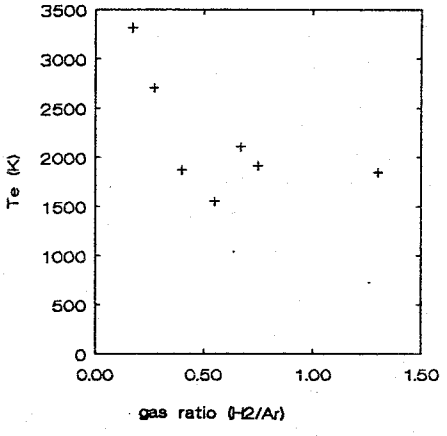


Fig. 3a H_2/Ar flow ratio vs. n_e
The pressure is 0.5 Torr, I_{arc} = 75 A

3b H_2/Ar flow ratio vs. T_e

Increasing the gas ratio H_2/Ar at constant pressure shows the same effect as increasing pressure (fig. 3a, b). This suggests that rather than the overall pressure, the hydrogen partial pressure determines the recombination rate. Further in this paper we present an overview of the mechanisms which might be responsible for this. We note that below p = 0.4 Torr no measurements are available, since the probe became thermoemissive (red hot) at lower pressures. Above 0.4 Torr, the jet becomes less bright and shorter, which is in agreement with the quantitative electron density determination.

4 - Mass spectrometry

At the end of the vessel, 40 cm from the anode plate, positive ions are extracted through an extraction hole of 0.1 mm diameter. Here also pressure and gas ratio are the varied parameters. The ions detected are H^+, H_2^+, H_3^+, Ar^+, ArH^+, O^+, HO^+ and H_2O^+, where the latter three are due to residual water in the vacuum system. At the slightest (< 1%) addition of hydrogen to the argon plasma, all H_2^+, Ar^+, ArH^+, O^+, HO^+ and H_2O^+ disappeared, and only H^+ and H_3^+ remained. In the following we will concentrate on these ions. For a mixture of 0.5 SLM H_2 and 2.5 SLM Ar, the pressure dependence of H^+ and H_3^+ is given in fig. 4. The number of counts of H^+ shows a maximum at p = 0.3 Torr. In the range 0-0.3 Torr the number of H^+counts increases with pressure. This effect is known in pure argon experiments /1/, where an increase in electron density is found which is caused by reduction of the beam diameter with increasing pressure. As the electron fluence remains constant, the electron (ion) density increases. Apparently for the hydrogen argon mixture, a similar effect is present below p ~ 0.3 Torr. Above p = 0.3 Torr, the number of H^+ counts decreases, which is in agreement with the probe measurements on n_e. The recombination mechanism becomes effective at this pressure. The H_3^+ signal goes down monotonically with the pressure; the pressure dependence is larger than that of H^+ above 0.3 Torr. This will be explained later in this paper.

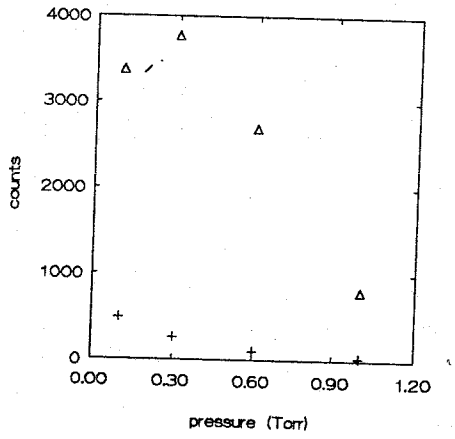


Fig. 4 H^+ (+) and H_3^+ (Δ) counts vs pressure p

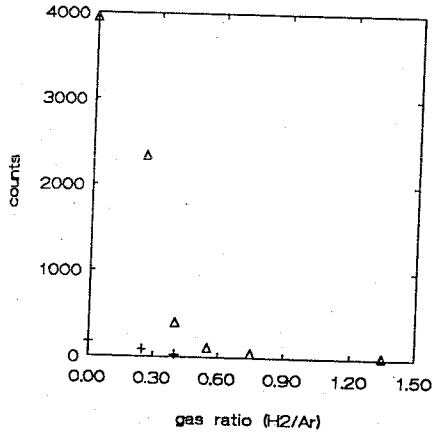


Fig. 5 H^+ and H_3^+ counts vs H_2/Ar gas ratio. Pressure p=0.5 Torr.

The influence of the hydrogen percentage on the detected ion signal (fig. 5) may at first sight be somewhat surprising: an increasing partial hydrogen flow results in a lower count rate for H^+ and H_3^+. Apparently the addition of a molecular gas leads to an enhanced decrease of the electron density; this will be explained by the mechanism of dissociative recombination which is only effective in molecular gases. At the given pressure (0.5 Torr) and position of the extraction hole (40 cm away from the plasma source) the residual hydrogen pressure, e.g. gas from the walls or impurities of the argon, already seems efficient to destruct ions. Any increase in hydrogen flux then enlarges the recombination rate.

Recombination processes

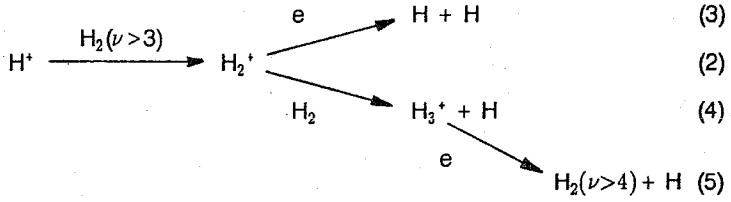
As an illustration we will first consider the influence of a very small percentage of hydrogen compared to the pure argon case. To that purpose consider an expanding plasma beam at a background pressure of 1 Torr, at typical values just after the shock disk of /1/: T_{gas} = 4000 K, $[Ar^+] = 10^{20}$ m^{-3}, $[Ar] = 2 \cdot 10^{21}$ m^{-3} and a flow velocity of 600 m/s /1/. If we consider the reaction

$$Ar^+ + H_2 \rightarrow ArH^+ + H \qquad (1)$$

we can calculate the Ar^+ destruction rate for a hydrogen percentage of for example 0.1 %. The rate coefficient for (1) is $\kappa \simeq 10^{-15}$ m^3s^{-1} for cold gas /5,7,8/. The recombination of ArH^+ with an electron is very efficient; at the given temperature dissociative recombination processes have typical rate coefficients of 10^{-13} m^3s^{-1}, moreover the electron density is still quite high. We introduce a destruction time t_{des} and a destruction length $x_{des} = v_{jet} \cdot t_{des}$ as the needed time respectively flow distance to decrease the Ar^+ ion density in the plasma to the 1/e value. For 1 *promille* H_2 partial pressure and given values for densities and flow velocity we can calculate t_{des} from

$$d[Ar^+]/dt = [H_2] \cdot [Ar^+] \cdot \kappa, \qquad t_{des} = (\kappa \cdot [H_2])^{-1}$$

which gives $t_{des} \simeq 0.5$ msec and $x_{des} \simeq 30$ cm. Mechanism (1) can thus be important at higher pressures to quench an argon plasma, even for a low partial molecular density of H_2.
Now consider a cascade arc with a hydrogen argon plasma close enough to LTE. There will be full dissociation and the particles will be ionized in order of the lowest ionization energy. Hydrogen will thus first be dissociated, then ionized, and only then argon can be ionized. The ionization degree at the end of the arc is typically 10%, so at 5% H_2 concentration there will hardly be any Ar^+ leaving the arc. In the case of a gas ratio H_2:Ar of 1:6 we can neglect reaction mechanisms involving Ar^+ in the expansion. Direct atomic recombination and three particle recombination are also negligible at the electron densities in the expanding plasma. We first give an overview of the remaining recombination and associative processes in a hydrogen plasma.



A crucial step in this mechanism for dissociative recombination is reaction (2): for cold hydrogen gas this reaction has a very low rate coefficient, since the process is endothermic. In recent experiments /6/ though strong evidence is found, that in cold gas the charge exchange takes place in two steps: first the molecule is vibrationally excited to $\nu>3$, then charge may be exchanged. For molecules that are already vibrationally excited to $\nu>3$, the rate coefficient can be expected to be much larger. We assume a cross section for reaction (2) of 10^{-18} m^2 and a rate coefficient of 10^{-14} m^3s^{-1}, which are typical values for charge exchange. We now give an overview of the reaction rates for the processes in fig. 6.

Table 1 reaction mechanisms and rate coefficients for $T_e \simeq 0.25$ eV.

reaction mechanism	κ (m^3/s)	reference
(2) $H^+ + H_2(\nu>3) \rightarrow H_2^+ + H$	10^{-14}	
(3) $H_2^+ + H_2 \rightarrow H_3^+ + H$	$3 \cdot 10^{-15}$	/7,8/
(4) $H_2^+ + e \rightarrow H^* + H$	10^{-13}	/7,8/
(5) $H_3^+ + e \rightarrow H_2(\nu>4) + H$	$\frac{1}{2} \cdot 10^{-13}$	/7,8/

Essential for this recombination mechanism is a sufficiently large population of $H_2(\nu>3)$. There are two sources of vibrationaly excited hydrogen molecules. First at the periphery of the arc the heavy particle temperature is lower and residual, hydrogen molecules must be expected in the emerging plasma beam. The vibrational temperatures will be in the order of 0.5 eV-1 eV, so an appreciable fraction will be vibrationally excited. The second source of vibrationally excited molecules is the association of H atoms at the wall of the expansion vessel. There are indications that this association leads to vibrationally excited molecules /9/. Also the background H_2 molecules will be heated by the plasma in the expansion chamber to temperatures of 0.2 - 0.4 eV /10/. So a vibrationally excited H_2 density of 0.1 % at 0.5 torr at 3000 K corresponds to a density of $1.5\ 10^{18}$

m^{-3}, which can be regarded as a conservative estimate. From table 1 /7,8/ it can be seen, that if the electron density is more than about 3% of the molecular hydrogen density, H_2^+ will be destroyed by dissociative recombination, else reaction (3) and (5) dominate. This explains why no H_2^+ is detected with the mass spectrometer: at 40 cm from the arc, the electron density is low (the plasma jet cannot be seen there any more) and all H_2^+ is converted to H_3^+. We can also explain the strong decrease of the H_3^+ signal with pressure in fig. 4: from H^+ and thus the conversion to H_3^+ the production of H_2^+ is slowed down by a decrease of the density of $H_2(\nu>3)$. Further we note that with transit times in the order of a few times 10^{-3} s dissociative recombination becomes too slow to be effective for electron densities lower then $\sim 10^{16}$ m^{-3}. These are the densities observed for molecular plasmas.

5 - Conclusions

The behavior of the electron density as measured with a Langmuir probe, and of the ion count rates as measured with an ion mass spectrometer, indicates that molecular recombination processes are important in the expanding plasma. The mechanism presented in this paper can explain the experimental results. It seems preliminary, though, to draw definitive conclusions. More experimental work is desirable to test the made assumptions in particular the vibrational excitation of H_2 molecules. Having made this reservation, some remarks can be made on the impact of the molecular processes on the design of a proton source. To preserve ionization degree, it is essential to keep the molecular hydrogen density as low as possible. At the side of the source this demands a high dissociation degree, to be achieved by sufficient power input in the arc and optionally by drawing current to an auxilliary anode in the vacuum chamber. The latter is to reduce the effect of recombination of hydrogen at the wall of the arc channel. In the expansion chamber the molecular hydrogen density can be reduced by lowering the background pressure, by magnetic field enclosure of the beam or by baffling.
A final remark should be made concerning the formation of negative ions by electron impact on vibrationaly excited molecules. This reaction is about 10 % of the charge exchange reaction (2). Therefore significant H^- formation must be expected; this will also be subject of further study.

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References

/1/ G.M.W. Kroesen, 'Plasma Deposition: Investigations on a New Approach', Thesis Eindhoven University of Technology, The Netherlands (1988).
/2/ P.K. Bachmann, J.J. Beulens, G.M.W. Kroesen, H. Lydtin, D.C. Schram, and D.U. Wiechert, Proc. '3rd Conf. on Surface Modification Technologies', Neuchatel, 1989.
/3/ G.J. Meeusen, A.T.M. Wilbers, C.J. Timmermans, and D.C. Schram, to be published.
/4/ P.M. Vallinga, 'Vth International Symposium On the Production and Neutralization of Negative Ions and Beams', Brookhaven, NE, USA, 1989.
/5/ Kenichiro Tanaka, Jean Durup, Tatsuhisa Kato and Inosuke Koyano, J. Chem. Phys. 74, (1981) 5561.
/6/ G. Nieder, M. Noll and J.P. Toennies, J. Chem. Phys. 87 (1987) 2685.
/7/ H. Gutbier, Z. Naturforschg 12a (1957) 499.
/8/ R.K. Janev, W.D. Langer, K. Evans Jr., D.E. Post Jr., Elementary Processes in Hydrogen-Helium Plasmas, Springer Verlag, Berlin, 1987.
/9/ P.J. Eenshuistra, R.M.A. Heeren, A.W. Kleyn, and H.J. Hopman, Phys. Rev. A40 (1989) 3613-3625.
/10/ J. Koulidiati, A. Czernichowski, J.J. Beulens, et D.C. Schram, Proc. '1st European Congress on Thermal Plasma Processes and Materials Behavior at High Temperatures', Odeillo, France, sept. 12-14 1990.