A cascade arc atomic hydrogen source

JOURNAL OF HIGH TEMPERATURE CHEMICAL PROCESSES
Colloque, supplément au n°3, Vol 1, Septembre 1992

A cascade arc atomic hydrogen source

M. J. de Graaf, Z. Qing, H. W. A. Tolido, M. C. M. van de Sanden and D. C. Schram

University of Technology, Department of Physics Eindhoven, The Netherlands

Abstract

An expanding cascade arc plasma is investigated as an atomic hydrogen source. From measurements on power input and heat losses the efficiency and dissociation degree can be estimated. At an energy efficiency of typically 30% the source yields a dissociation degree of 0.3 to close to full dissociation.

1 Introduction

In various plasma processing applications atomic hydrogen is an important specie. Examples are plasma deposition of carbon [1] and silicon [2] layers, where hydrogen radicals remove the weaker bonds. Another application is found in the treatment and conservation of metal archeological artefacts [3]. It has been shown that corrosion resistance of artefacts is considerably improved after a hydrogen plasma treatment. Finally, the number of bulk chemical processes where hydrogen radicals could be used is enormous. Therefore an efficient atomic hydrogen source is interesting. Here we present such a source.

2 The cascade arc plasma source

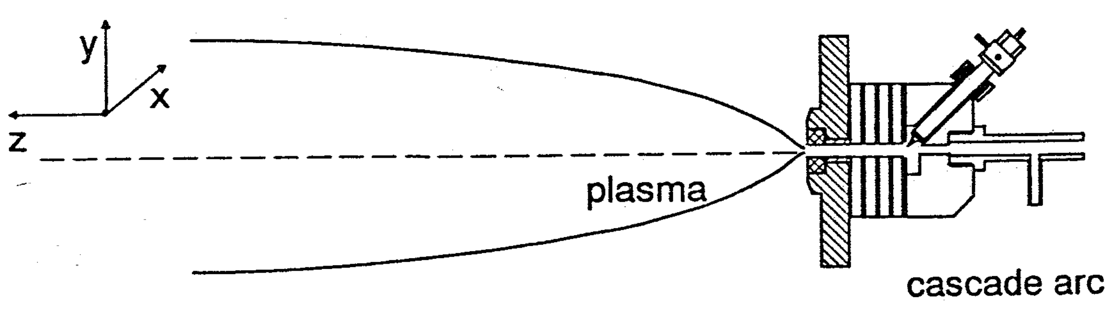

Figure 1: The experimental setup

A cascade arc is used to generate the source plasma, where the hydrogen atoms are produced (Figure 1). Between three of cathode tips and an anode plate a gas discharge maintained. To stabilize the discharge it is thermally confined to a narrow channel by a stack of water cooled copper plates with a central bore of 4 mm. Gas flows in at the cathode side and at the anode side the generated plasma is allowed to expand into a low pressure reactor. Requirements for the source are a hydrogen gas flow of 1-10 slm (standard liter per minute), a power input of 5-30 kWatt (35-75A, 150-400V) and a cooling water flow of 5-10 l/min. The pressure in the cascade arc is in the range of 0.05 to 0.5 bar.

3 Experiments

The source has been operated at hydrogen gas flows of 3, 6 and 9 slm at two currents, 35 and 50 A. These series of settings have been measured for a three and a four plate cascade arc. The heat transfer to the cooling water of the cathodes, the anode and each plate were measured. This was done by an array of water flow meters and temperature sensors at the i[illegible] and outlet side. Measurement of the total arc current and of the voltage at each part of the arc enabled a determination of the ohmic power input along the plasma axis. The pressure in the reactor could be varied between 0.1 and 20 mbar.

4 Calculations

In order to investigate the effectiveness of the cascade arc source to dissociate H_2-gas, measurements have been performed on the power balance in the cathode, anode and cascade plates. The efficiency η is defined by

$$\eta = \frac{P_{\text{plasma}}}{P_{\text{Ohmic}}} = 1 - \frac{P_{\text{cool}}}{P_{\text{Ohmic}}} \tag{1}$$

where P_{plasma} is the power which is effectively coupled into the plasma, P_{Ohmic} the ohmic input (total electric power input) and P_{cool} the heat loss to the cooling water. The efficiency is determined for the cathode, anode and each plate. P_{Ohmic} is calculated from the arc current and the voltage drop between adjacent plates. P_{cool} is determined by measuring the flow and the increase in temperature of the cooling water.

The dissociation degree of the particle flow leaving the cascade arc is defined by

$$\beta = \frac{\Phi_H}{2\Phi^0_{H_2}} \tag{2}$$

where Φ_H is the atomic hydrogen particle flow and $\Phi^0_{H_2}$ is the molecular gas flow at the arc inlet. This is the fraction of the incoming hydrogen *mass* that is dissociated. The ionization degree is in a similar way defined in relation to the inlet gas flow,

$$\alpha = \frac{\Phi_{\text{ion}}}{2\Phi^0_{H_2}} \tag{3}$$

with Φ_{ion} the total ion flow.

Starting from the analysis of the energy balance analysis, an upper and lower limit for the dissociation degree can be estimated. The power which is effectively coupled into the plasma is used to heat, dissociate and ionize the hydrogen content,

$$P_{\text{plasma}} = P_{\text{heat}} + P_{\text{diss}} + P_{\text{ion}} \tag{4}$$

The three terms at the right hand side will be regarded succesively. The acceleration energy of the plasma is included in the thermal energy of the particles. An upper limit estimate of the energy needed for heating is made as follows. Consider the thermal energies of the different species molecules, atoms, ions and electrons,

$$P_{heat} = \Phi_{H_2} \cdot \frac{5}{2} k\Delta T_{H_2} + \Phi_H \cdot \frac{3}{2} k\Delta T_H + \Phi_{\text{i}} \cdot \frac{3}{2} k\Delta T_{\text{i}} + \Phi_{\text{e}} \cdot \frac{3}{2} k\Delta T_{\text{e}} \tag{5}$$

The average temperature of the molecules leaving the arc is certain to be below 0.4 eV (4500 K) because above this temperature dissociation is almost complete [4]. The atoms, ions and

T, °K	H_2	H	H^+	H^-	e
300	2,7 (19)	—	—	—	—
1 000	8,1 (18)	—	—	—	—
2 000	4,05 (18)	6,5 (15)	—	—	—
3 000	2,3 (18)	3,9 (17)	—	—	—
4 000	4,7 (17)	1,54 (18)	—	—	—
5 000	3,7 (16)	1,58 (18)	—	—	—
6 000	5,05 (15)	1,34 (18)	6,1 (13)	9,4 (10)	8,1 (13)
8 000	3,5 (14)	1,0 (18)	2,45 (15)	9,4 (11)	2,46 (15)
10 000	6,8 (13)	7,7 (17)	1,9 (16)	3,2 (12)	1,92 (16)
12 000	—	5,3 (17)	7,1 (16)	5,4 (12)	7,1 (16)
14 000	—	2,8 (17)	1,48 (17)	—	1,48 (17)
16 000	—	1,06 (17)	2,0 (17)	—	2,0 (17)
18 000	—	3,45 (16)	2,1 (17)	—	2,1 (17)
20 000	—	1,15 (16)	1,97 (17)	—	1,97 (17)

Table 1: Plasma composition as a function of temperature

electrons are assumed to be at an average temperature of 1 eV (11500 K). This is a typical temperature for the hot center of the plasma channel [5]. The power used for dissociation is presented by

$$P_{\text{diss}} = 2 \cdot \beta \cdot \Phi^0_{H_2} \cdot E_{\text{diss}} \tag{6}$$

where E_{diss} is the dissociation energy per atom, so half the energy needed to dissociate a molecule. For ionization the expression is similar,

$$P_{\text{ion}} = 2 \cdot \alpha \cdot \Phi^0_{H_2} \cdot E_{\text{ion}} \tag{7}$$

Combining equation (2)-(7) and substituting the values of the various energies we can find the expression

$$\frac{P_{\text{plasma}}}{\Phi^0_{H_2}} = 1 + 6.5\beta + 32.2\alpha \tag{8}$$

where the power is given in eV/sec and the flow in particles/sec. Table 1 shows that in full equilibrium plasma ionization only occurs after full dissociation has taken place. However, in the cascade arc there is no thermal equilibrium over the plasma radius. To be able to estimate a dissociation degree, according to formula (8) the ionization degree must be known. For a lower limit estimate, a comparison with an argon plasma at similar circumstances can be made [5]. In the arc center the temperature is 1 eV as well in argon as in hydrogen. There the ionization degree is typical 5-10% and for molecular gases the dissociation is complete. The situation is different closer to the wall; in monoatomic gases the T_e profile is rather flat and only close to the wall a transition layer occurs. In hydrogen however the conductive high T_e plasma channel is considerably smaller due to heat conduction. In the now extended wall layer a substantial residual molecule density may exist; this in fact is the very reason why dissociation degree is not 100%. Hence the smaller the central hot channel the more escape of molecules and the smaller the average ionization degree averaged over the arc exit area. A first information on the effective surface of the central, ionized channel comes from the plasma resistance. The conductivity in the plasma is only high in the central, high T_e channel. Here it is governed by Coulomb e-i scattering and is proportional to $T_e^{3/2} \ln\Lambda$, in which Λ is the Coulomb logarithm[6]. As the electron temperature is 1 eV both for argon and hydrogen the change in resistance is fully caused by a change of the cross section of the conducting channel, i.e. the hot plasma center. Experiments show a four times larger voltage drop in a hydrogen plasma than in an argon plasma. For the overall ionization degree in a hydrogen plasma this would mean a four times smaller value than in a corresponding argon case. As a safe high estimate only a factor two lower ionization is taken. At the used flows, the cross section averaged ionization degree for argon is less than 5%. For the hydrogen case the lower limit of the calculated dissociation degrees and atomic hydrogen flows are obtained by assuming 2.5% ionization, the higher limit by assuming no ionization.

5 results

Figure 2 shows for a three and a four plate arc the total Ohmic power input, the heat loss to the cooling water and the power that remains in the plasma as a function of flow. At increasing flow the Ohmic power input increases. This increase goes fully to the plasma; there is no significant increase in heat loss to the cooling water. At the higher current, 50 A, the magnitudes of the Ohmic input, of the heat loss and of the remaining power to the plasma all are higher than at 35 A. The ratios between these three quantities does however not change significantly. More current therefore means a higher power input without a change in efficiency. Figure 3 shows the efficiency according to equation (1) calculated from the data of figure 2. It shows an increasing efficiency at increasing gas flow. The four plate arc shows a lower efficiency than the shorter one. The influence of the current is not significant. The dissociation degree, calculated from equation (8) is given in figure 4. It shows that at the lowest flows the dissociation degree has the highest values. The power input per slm hydrogen gas is then maximum. The point in figure 5 that indicates full dissociation is for some reasons inaccurate: first, the efficiency is very low and therefore the determination of P_{plasma} is inaccurate. Second, at such low flow and high power input the the ionization degree of the plasma may exceed the estimated maximum of 2.5%. The atomic hydrogen flow emanating from the cascade arc source is plotted versus gas flow in figure 5. It shows that although the dissociation degree is highest at low gas flows, this fact is more than compensated for by the larger gas flow; maximum H^0 flow is reached at high flow and high current.

6 Discussion

The efficiency of the cascade arc as an atomic hydrogen source increases with increasing gas flow and current. The four plate arc gives a higher dissociation degree than the three plate arc, however, the efficiency goes down. Therefore, to obtain a higher dissociation degree, an increase in current is more appropriate than an increase in arc length. Furthermore, it is mentioned that at lower gas flows the ionization degree is expected to be higher than at higher gas flows. As a consequence, it is likely that the dissociation degree at low gas flows is closer to the estimated lower limit (2.5% ionization assumed) and at high gas flow closer to the estimated no ionization limit. The cascade arc source that was used in the here presented experiments has over the last two years been operated for over 1000 hours without any substantial damage. During this period, operational conditions have changed many times and the discharge has been started for hundreds of times. These facts give great confidence that the lifetime of the source at stable operation conditions will be very long.

Acknowledgements

The authors like to thank M.J.F. van de Sande and A.B.M. Hüsken for their technical support. This programm has been made possible by financial support of SHELL Recherche and the Foundation Fundamenteel Onderzoek der Materie.

References

[1] G.M.W. Kroesen, D.C. Schram and M.J.F. van de Sande, Plasma Chem. & Plasma Proc. **10** (1990), 49-69 .

[2] A.T.M. Wilbers, G.J. Meeusen, M. Haverlag, G.M.W. Kroesen and D.C. Schram, Thin Solid Films, **204** (1991) 59-75

[3] S. Veprek, J. Patscheider and J. Elmer, Plasma Chem. & Plasma Proc. **5** (1985), 201-209

[4] N.B. Vargaftik, "Tables on the thermophysical properties of liquids and gases: in normal and dissociated states", 2nd edition, Hemisphere publ. comp. (Wiley), Washington, 1975.

[5] J.J Beulens, M.J. de Graaf, G.M.W. Kroesen and D.C. Schram, Proc. Materials Research Soc. Spring Mtg., Vol. 190, San Fransisco (Materials Research Society, Pittsburgh, 1990).

[6] S.I. Braginskii, in Rev. on Plasma Physics, **1**, 205 (1965).

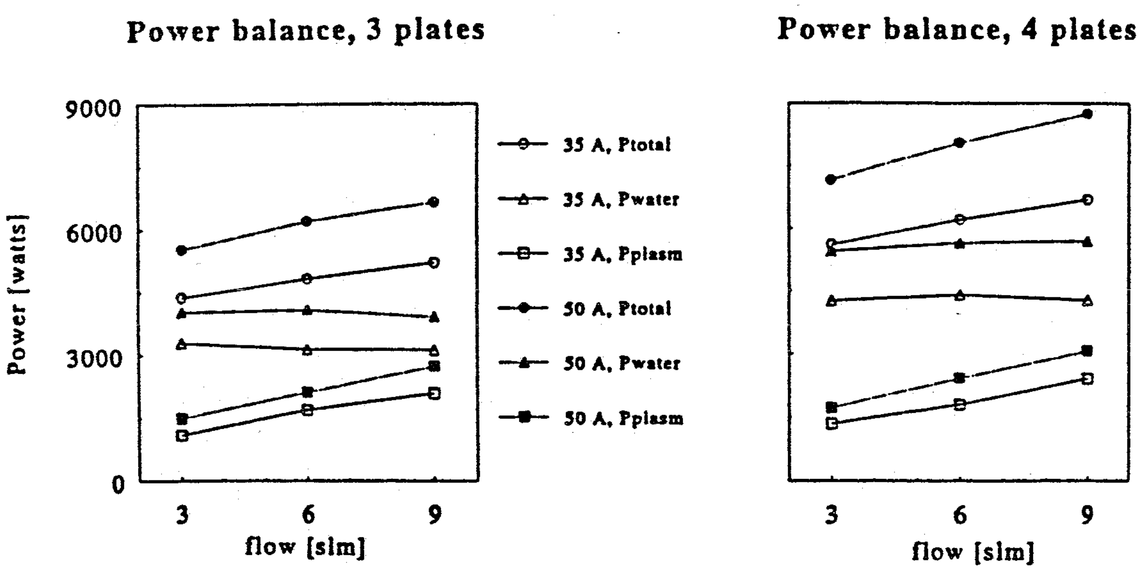

Figure 2: The power balance in the cascade arc source.

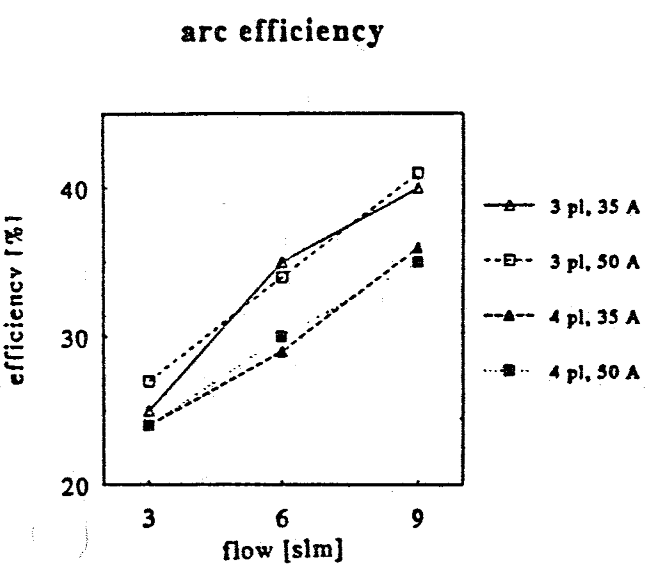

Figure 3: The efficiency of the source

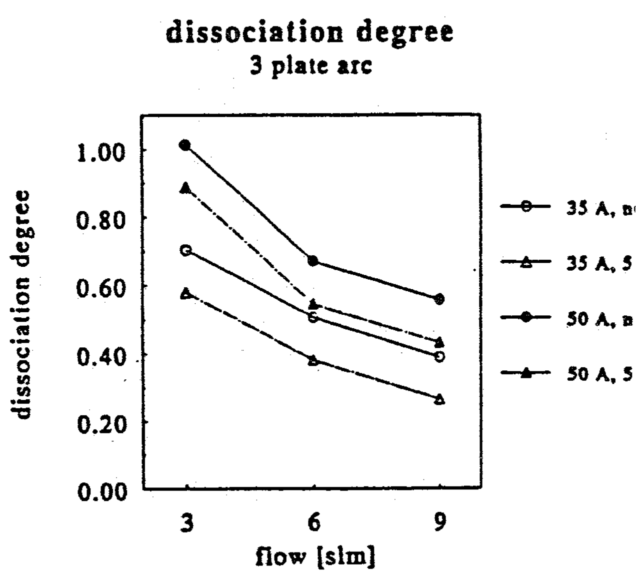

Figure 4: The dissociation degree

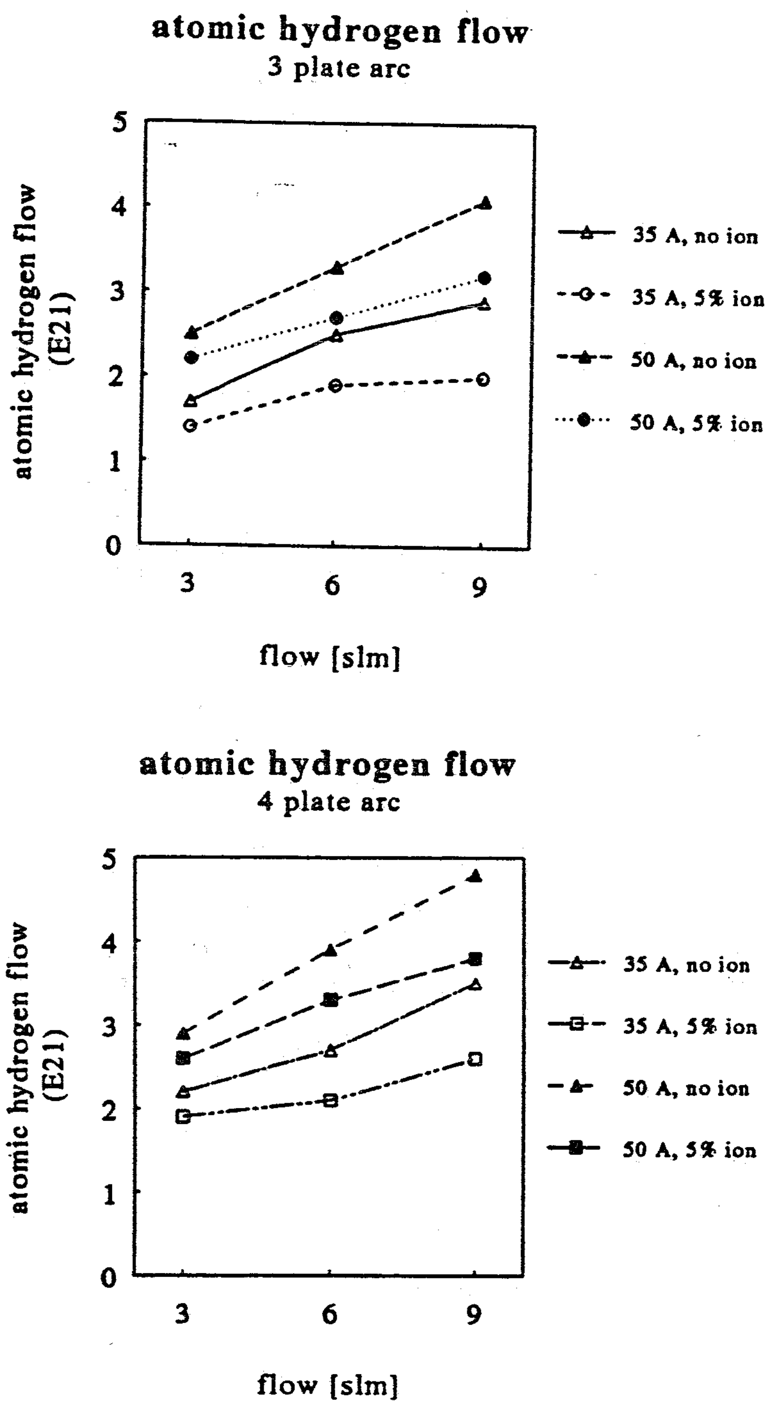

Figure 5: Upper and lower estimates for the atomic hydrogen flow from the arc exit.