Wall-Association Processes in Expanding Thermal Hydrogen Plasmas

S. Mazouffre, P. Vankan, W. M. M. Kessels, R. Engeln, M. C. M. van de Sanden, and D. C. Schram

***Abstract*—The amount of ions and atomic radicals contained in an expanding thermal hydrogen plasma, which is produced by a wall-stabilized dc arc, depends on the source nozzle geometry and material. The nature of the radiation emanating from the plasma jet is also influenced by the nozzle properties. In the light of experimental data obtained by means of laser-aided diagnostics, these striking facts can be explained by the wall-association processes of hydrogen atoms to form vibrationally excited hydrogen molecules.**

***Index Terms*—Expansion, hydrogen, plasma, recombination, wall.**

AN EXPANDING thermal plasma created by a cascaded arc, see Fig. 1, is a perfectly suited plasma medium for chemical processing in view of the following specific features [1]:

1) high dissociation and ionization degree in the arc channel ($p \approx 0.5$ atm) combined with a supersonic speed leads to a high reactive particle flux when a mixture of atomic and molecular gases is used;
2) low electron temperature in the jet ($T_e \approx 0.2$ eV, due to the quasi-adiabatic cooling in the supersonic flow domain) and the low sheath voltage allow for complex molecules to survive (no electron and ion induced damage);
3) low-pressure environment (10 to 100 Pa) results in a good mixing between particles present in the background (e.g., injected precursors) and high kinetic energy particles contained in the plasma jet.

Such plasma jets have proven to be successful in the field of surface modifications [1], like in deposition of amorphous hydrogenated silicon (a-Si:H) [2].

The visible light emission of an expanding Ar-H_2 plasma created by a cascaded arc with a straight copper (Cu) nozzle is shown in Fig. 1. Note that all photographs have been taken with an ordinary digital camera (no filter). The light originates from electron recombination processes and it is, therefore, a sign for the presence of ions. When operated on a 6:1 Ar–H_2 mixture, the hydrogen dissociation degree at the arc exit is around 45% as determined from two-photon absorption laser induced fluorescence (TALIF) measurements [3]. This makes such a plasma jet a high chemical potential jet.

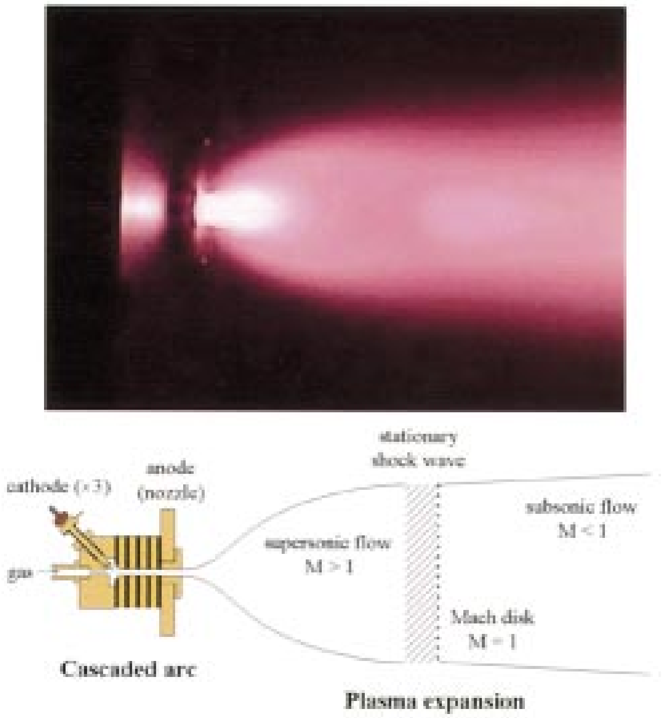


Fig. 1. Picture of an expanding argon/hydrogen plasma produced by a cascaded arc (3 standard liters per minute (slm) Ar flow, 0.2 slm H_2 flow, 55 A, 100 Pa background pressure) and simplified structure of a plasma expansion. The light originates mainly from three-particle recombination of Ar^+ and H^+ and from dissociative recombination of ArH^+. The dark zone visible in the jet corresponds to the region upstream of the shock wave where the charged particle density is too low to lead to a significant amount of radiation.

When an arc with identical nozzle design is burned on pure hydrogen, the difference is drastic. First, as can be seen in Fig. 2(a), the plasma flowing out of the nozzle is relatively dark, only faint bluish light remains. Second, as measured by Thomson scattering, the ionization degree α at the arc outlet is extremely low $(\alpha < 10^{-4})$ [4] whereas $\alpha \approx 10\%$ in the arc channel. Third, coherent antistokes raman scattering (CARS) measurements reveal that most of H_2 molecules leaving the arc are in the $v = 0$ vibrational state of the electronic ground state [4]. Fourth, the dissociation degree at the arc exit measured by TALIF is around 4% [5], whereas the plasma is almost fully dissociated inside the source.

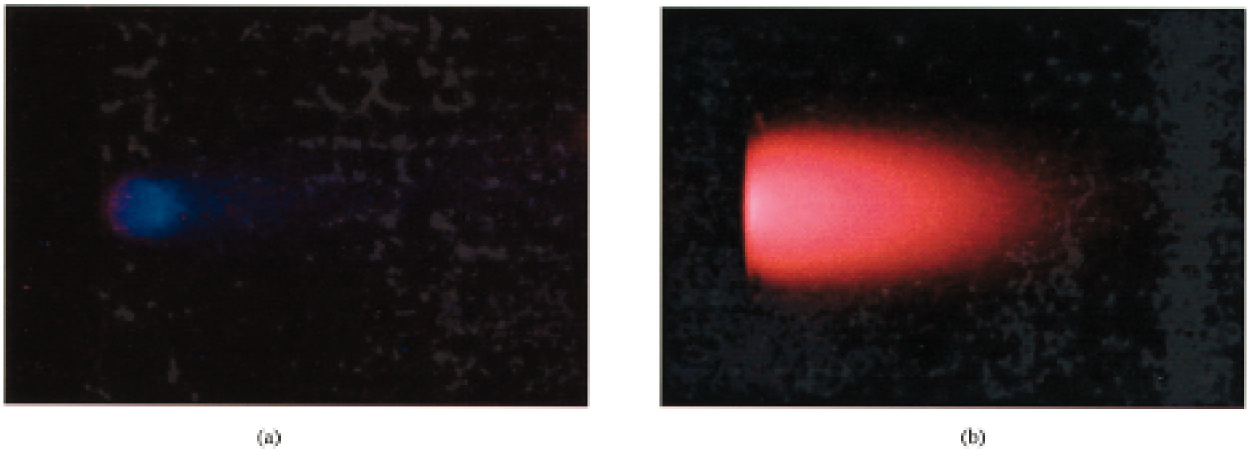
Apart from a change in the gas mixture injected in the arc, surprisingly, a modification in the nozzle geometry or material has also a strong influence on both the light emission and the dissociation degree of the plasma emerging out of the arc. As shown in Fig. 2, changing from a straight to a divergent nozzle

---

Manuscript received July 6, 2001; revised November 13, 2001. This work was supported in part by the Dutch Organization for Scientific Research (NWO) and by the Euratom Foundation.

The authors are with the Center for Plasma Physics and Radiation Technology, Department of Applied Physics, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands (e-mail: r.engln@phys.tue.nl).

Publisher Item Identifier S 0093-3813(02)03325-8.



(a) (b)

Fig. 2. Light emission of a hydrogen plasma, produced by a cascaded arc, expanding into a 100 Pa pressure environment (55A, 2.5 slm H_2 flow). A straight nozzle is used in the left picture, whereas a divergent (45°) nozzle is used in the right picture. In both cases, the nozzle is made of copper. The origin of the blue light is unknown, but it may originate from recombination of H^-. The red light (Balmer-α radiation) results from recombination of H^+ and H_2^+. The existence of a "dark" plasma jet may also be a sign for the presence of H_3^+. When a straight aluminum nozzle is employed, the light emission is similar to (a).

TABLE I

AMOUNT OF H ATOMS MEASURED BY TALIF IN THE SUBSONIC DOMAIN OF THE EXPANSION (ON THE JET AXIS, $z = 200$ mm) FOR DIFFERENT NOZZLE GEOMETRY AND MATERIAL. THE EXPERIMENTAL SETTINGS ARE KEPT CONSTANT: 55 A, 2.5 slm H_2 FLOW, 100 Pa BACKGROUND PRESSURE

nozzle	45°, Cu	straight, Cu	straight, Al
n_H (m^{-3})	3.6×10^{19}	6.0×10^{19}	1.4×10^{20}

modified the nature of the emitted radiation. In the case of a divergent nozzle, see Fig. 2(b), the observed red light (Balmer-α transition) is connected with the existence of a large amount of positive ions. The quantity of H atoms generated by the cascaded arc is also affected by the nozzle properties, as can be seen in Table I. For instance, the use of aluminum (Al) as nozzle material leads to a higher H atom density than with Cu.

A way to explain the effect of the arc nozzle design on the production of ions and atomic radicals, and on the subsequent light generation, is to consider wall-association processes inside the nozzle [5]. Indeed, no energy is supplied through the nozzle and, as a consequence, the recombination of H atoms at the wall to form vibrationally excited $H_2(v, J)$ molecules is favored. Such molecules can easily interact with protons and electrons and thus strongly affect the ion content.

The probability γ for recombination of H atoms, and the subsequent release of $H_2(v, J)$ in the gas phase, is much higher on Cu $(\gamma \approx 1)$ [5] than on Al $(\gamma \approx 0.3)$ [6] that explains the difference in H atom density in the plasma jet. Note that a thin layer of oxide can easily be formed on an aluminum surface that leads to an extremely low loss probability: $\gamma \approx 0.002$ on AlO_x [6]. The quasi-absence of visible light and the low ionization degree in the case of a straight Cu nozzle is believed to be the result of the quick recombination of H_2^+. These molecular ions arise from charge exchange reaction between $H_2(v, J)$ formed at the wall and H^+ (the main ion in the arc channel), and they dissociatively recombine before leaving the arc [5].

The large amount of red light and the low H atoms content observed in the case of a 45° Cu nozzle is not yet fully understood. Turbulent mixing in the divergent section of the nozzle may lead to an efficient destruction of H atoms. However, the expected large amount of $H_2(v, J)$ molecules should make the light disappear, which seemingly is not the case.

Wall-association processes are certainly complex (and not yet well grasped) but they must be taken into account when considering plasma-assisted chemistry. As shown in this contribution, they can drastically influence the characteristics of the created plasma, and thus the downstream chemistry. In addition, as shown elsewhere [3], [5], such processes can to a large extent control the transport mechanisms of reactive species in plasma expansions.

REFERENCES

[1] D. C. Schram, S. Mazouffre, R. Engeln, and M. C. M. van de Sanden, "The physics of plasma expansion," in *Atomic and Molecular Beams*, R. Campargue, Ed. New York: Springer-Verlag, 2001, p. 209.

[2] W. M. M. Kessels, R. J. Severens, A. H. M. Smets, B. A. Korevaar, G. J. Adriaenssens, D. C. Schram, and M. C. M. van de Sanden, "Hydrogenated amorphous silicon deposited at very high growth rates by an expanding Ar-H_2-SiH_4 plasma," *J. Appl. Phys.*, vol. 89, pp. 2404–2413, 2001.

[3] S. Mazouffre, M. G. H. Boogaarts, J. A. M. van der Mullen, and D. C. Schram, "Anomalous atomic hydrogen shock wave pattern in a supersonic plasma jet," *Phys. Rev. Lett.*, vol. 84, pp. 2622–2625, 2000.

[4] R. F. G. Meulenbroeks, R. A. H. Engeln, J. A. M. van der Mullen, and D. C. Schram, "Coherent anti-Stokes Raman scattering performed on expanding thermal arc plasmas," *Phys. Rev.*, vol. E 53, pp. 5207–5217, 1996.

[5] S. Mazouffre, P. Vankan, R. Engeln, and D. C. Schram, "Influence of surface chemistry on the transport of H atoms in a supersonic hydrogen plasma jet," *Phys. Plasmas*, vol. 8, pp. 3824–3832, 2001.

[6] A. D. Tserepi and T. A. Miller, "TALIF of H atoms: A probe for heterogeneous processes in hydrogen plasmas," *J. Appl. Phys.*, vol. 75, pp. 7231–7236, 1994.