HYDROGEN AND OXYGEN EVOLUTION IN UNDERWATER PLASMA CUTTING

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ABSTRACT

Measurements of hydrogen and oxygen evolution rates from underwater plasma cutting of carbon steel are described. Evolution rates and ratios are such that thermal dissociation of water and reactions with steel are the most likely formation mechanisms rather than electrolysis. Effluent gas compositions are compared with literature data on flammability limits.

1. INTRODUCTION

Plasma cutting of metals can be done underwater for noise and fume suppression and more recently has become of interest as a potential tool for underwater fabrication and maintenance offshore. A question which arises in evaluating this latest application is whether significant amounts of hydrogen and oxygen could be evolved in the process and, if so, whether these could form a flammable mixture. The evolution of hydrogen from water/plasma/metal interactions is also of interest in the general area of wet underwater welding. No systematic studies of gas evolution inunderwater plasma cutting have been reported. The few quantitative data on composition and rates by Adorni et al(1) appear not to correspond to steady-state conditions. Madatov(2) attributed the generation of hydrogen to electrolysis but gave no data on evolution rates.

The present paper describes some results from a detailed study(3) which covered the influence of several operating parameters, such as electrical power, speed, cutting gas flow rate, workpiece composition and torch design factors.

2. EXPERIMENTAL

Cutting runs were done in a tank with the torch held stationary in the vertical position and workpieces moved horizontally at controlled speeds (Figure 1). Water depths were around 1 metre. Power was obtained from two d.c. welding generators connected in series to give an open circuit voltage of 165 volts. The torch was designed to allow wide variation in electrode geometry and flow configurations. Argon was used as plasma feed gas to minimise voltage requirements and minimise changes in workpiece composition. Some combinations of current and speed do not necessarily correspond to optimum cutting conditions but were used to establish firm trends over a wide range of conditions.

As the main interest is in the characteristics of gas which might accumulate in equipment being cut, the evolved gas composition and flow rates were measured well downstream where the plasma effluent had reached near thermal equilibrium with surrounding water. Although problems associated with sampling from a high temperature plasma stream are thereby eliminated, the choice of analytical instrumentation and sampling technique still poses some problems because of the need to obtain steady-state data over relatively short run times, around 30-120 sec. Other practical problems to be overcome are the separation of liquid water from the sample stream, avoidance of any air ingress into the sample, and maintenance of a constant sample flow rate independent of plasma gas flow rate. The sampling system finally developed to overcome these problems is shown diagramatically in Figure 1. Theoretical and experimental studies(3) showed that any absorption or stripping effects in the tank water had a negligable effect on measured gas composition in cutting experiments. Oxygen concentration was measured by two instruments, a paramagnetic oxygen analyser and a polarographic instrument. Response times of these instruments were around 8 secs for 90% of a step change. For hydrogen, a commercial flammable gas detector operating on an electro-catalytic principle was modified to increase its response rate.

3. EXPERIMENTAL RESULTS

The influence of several parameters on hydrogen and oxygen evolution have been studied but it is only possible here to describe some of the main trends. Data here is for cutting of carbon steel (grade EN3B) in fresh water, results for other materials will be described separately.

Electrical power input (VxI) has a major influence on hydrogen evolution rate but, rather surprisingly, oxygen evolution rate is nearly independent of power. The hydrogen/oxygen ratio therefore increases with power input when other parameters are kept constant. These trends are exemplified in Figures 2a, 2b.

Increasing the argon flow rate in cutting increases the evolution rates of both hydrogen and oxygen as shown in Table 1. Hydrogen evolution rate has been standardised with respect to power input to eliminate the effect of changes in power with argon flow. Because oxygen evolution is more sensitive to argon flow, the H_2/O_2 ratio decreases with increase in argon flow rate.

It was thought possible that the increase in hydrogen and oxygen evolution was due to increased water entrainment and dissociation and so the influence of argon flow pattern was studied. This flow pattern was changed by changing the injection mode inside the torch. Three injection modes were used:- axial, tangential at 60° to the forward axis, and tangential at 80° to the forward axis. Injection mode does influence H_2 and O_2 evolution rates as seen in Figure 3a. Corresponding H_2/O_2 ratios are in Figure 3b.

For non-transferred jets, current levels similar in magnitude to those for cutting could only be achieved by increasing the nozzle diameter, e.g. to 3.5mm for 170 amps. Then the specific hydrogen evolution rate, calculated after subtracting measured electrode power losses ($\approx$ 40%), was 0.89 $cm^3.kJ^{-1}$ and the H_2/O_2ratio 1.9. Placing an asbestos plate in front of the plasma jet, to part simulate a workpiece but avoid metal reactions, increased the hydrogen evolution to 1.77 $cm^3.kJ^{-1}$ and the H_2/O_2 ratio to 2.2.

4. DISCUSSION

Considering first the question of flammability of the effluent gas stream, a definitive statement on this cannot be made due to lack of data on the flammability limits for $Ar/H_2/O_2$ mixtures. Assuming such mixtures have similar limits to those for dry Ar/H_2/Air mixtures measured by VanHeiningen(4), then the effluent gases are, by themselves, non-flammable. If, however, those effluent gases containing more than about 4.5% hydrogen were mixed with certain proportions of air, then they would form mixtures which lie inside the flammable limit envelope for dry Ar/H_2/Air mixtures.

The mechanisms of formation of hydrogen and oxygen have not been fully resolved but the present results suggest that dissociation of water and reactions with the steel workpiece are most important. Conventional liquid phase electrolysis cannot account for the rates of evolution nor for the frequent divergence of the H_2/O_2 ratio from 2. For example a hydrogen evolution rate of 60 $cm^3.s^{-1}$ (Fig.2a) would, according to Faraday's Law, require a leakage current of over 500 amps. This is far in excess of the total arc currents used and would be accompanied by significant metallic corrosion.

Thermal dissociation of water entrained into the arc column seems inevitable and, given the possibility of rapid quenching of the resulting mixture in the bulk water or on cold metal, could lead to hydrogen and oxygen formation. This mechanism would account for the evolution of hydrogen and oxygen from the non-transferred plasma jet exhausting under water. The higher evolution rates obtained when the jet impinged on a non-reactive surface could be due to enhanced entrainment and/or quenching caused by the increased turbulence. In both cases the H_2/O_2 ratio was near to 2.0, deviations from 2.0 being possibly due to analytical errors as H_2 and O_2 concentrations were relatively low there.

Computer solution of the high temperature multicomponent equilibria for water/inert gas starting mixtures shows(3) that H_2/O_2 ratios greater than 2.0 can result from thermal dissociation alone. An example is given in Figure 4 for water and water/argon starting material. The basic reason for the deviation from 2 is the formation of OH at medium temperatures. Maintenance of a H_2/O_2 ratio greater than 2.0 on quenching would presumably require a substantial part of the OH to be conserved and this is difficult to envisage.

Because the plasma and associated gas stream will inevitably contain water and water dissociation products, numerous reactions appear to be possible between these and the hot steel workpiece and associated dross behind the workpiece(3). In addition, dissolution of hydrogen and oxygen species in the hot steel will almost certainly occur. The overall outcome is particularly difficult to analyse quantitatively because of the wide temperature range involved, say 1000-3200°K metal temperature, rapid temperature transients and presence of alloying constituents in the steel. Two general schemes could account for the occurrence of H_2/O_2 ratios substantially greater than 2:-

a) Formation of hydrogen and oxygen species by water entrainment and dissociation followed by preferential removal of oxygen by physical and/or chemical interaction with steel

b) Formation of hydrogen and oxygen species by water entrainment and dissociation plus additional hydrogen formation by the reaction:

$$Fe + H_2O \rightarrow FeO + H_2$$

and analogous reactions involving alloying constituents.

Calculations to be presented separately suggest that scheme (b) is more likely, but it is quite possible that both (a) and (b) contribute. It would appear that (a) and (b) or other processes which promote high H_2/O_2 ratios become less significant at high argon rates and/or low power levels.

5. CONCLUSIONS

Hydrogen and oxygen can be produced in underwater plasma cutting of carbon steel with an inert plasma feed gas. Comparison of effluent gas composition with literature data on flammability limits suggest that the effluent is probably not flammable by itself, but for some cutting conditions, could, on mixing with air, form flammable mixtures. H_2 and O_2 evolution rates and ratios cannot be accounted for by electrolysis and probably result from a combination of thermal dissociation of water and chemical reactions with steel.

ACKNOWLEDGEMENT

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Argon flowrate	$g.s^{-1}$	0.72	1.00	1.44
Average specific H_2 evolution rate	$(cm^3.kJ^{-1})$	2.15	2.59	3.17
Average O_2 evolution rate	$(cm^3.s^{-1})$	5.13	12.00	18.00
Average specific H_2/O_2 ratio	(W^{-1})	0.42	0.22	0.17

Table 1 : Dependence of Gas Evolution on Argon Flow Rate

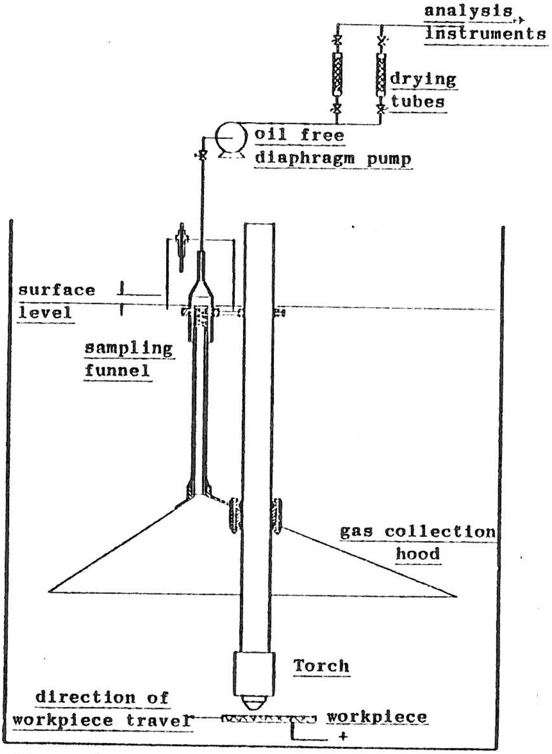
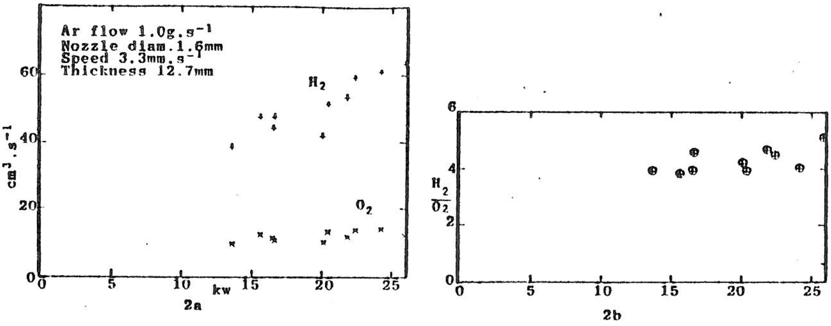


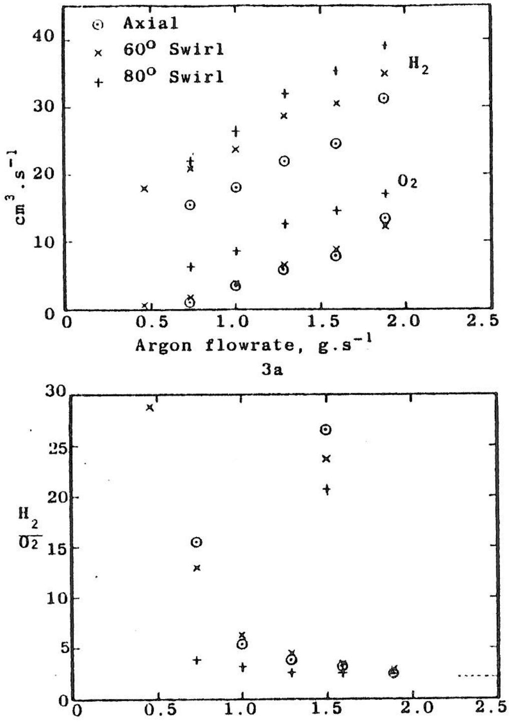
Figure 1: Schematic of cutting and sampling system.



2a

2b

Figure 2: Dependence of H_2 and O_2 evolution on electrical power a) Rates, cm^3.s^{-1}, b) H_2/O_2 ratio.



3a

3b

Figure 3a/b: Effects of argon flowrate and injection mode on gas evolution
a) Rates, $cm^3.s^{-1}$, b) H_2/O_2 ratio

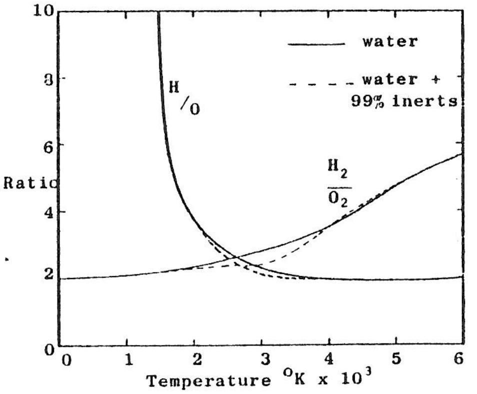


Figure 4: Temperature dependence of H/O and H_2/O_2 in equilibrium dissociated water