ELECTROLYTIC HYDROGEN WELDING RESULTED FROM WATER ELECTROLYSIS

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Summary

The hydrogen metal welding resulted from water electrolysis has the main advantage of hydrogen local producing necesary for smelting the weld metal and the base on.The hydrogen and oxygen electrochemically produced belong in stead to water electrolysis matter dominated by the energy yield which is too small to promote hydrogen as main fuel gas and this being the main alternative resurce to fossil combustibles.

Rezumat

Sudarea metalelor cu hidrogen rezultat din electroliza apei are principalul avantaj al producerii locale a hidrogenului necesar topirii metalului de adaus si a metalului de bază. Hidrogenul şi oxigenul produse pe cale electrochimică fac parte în schimb din problematica electrolizei apei dominată de randamentul energetic încă prea mic pentru a promova hidrogenul ca principalul gaz combustibil si prin aceasta ca principală resursa alternativă la combustibilii fosili.

Kurzfassung

Wasserstoffschweissen eines Basismetalls mit dem Zusatzmetall hat den besonderen Vorteil dass der Wasserstoff und der Sauerstoff lokal über Wasserelektrolyse erzeugt werden können. Der auf elektrochemischem Weg erzeugte Wasserstoff und Sauerstoff sind Teil der Problematik der Wasserelektrolyse . Diese Problematik ist hauptsächlich vom noch zu kleinem energetischen Wirkungsgrad dominiert was auch dazu führt daß der Wasserstoff noch nicht als wichtigstes Brenngas, als Alternative zu fosilen Brennstoffen, eingesetzt werden kann.

Hydrogen metal welding

Hydrogen is an almost perfect fuel gas for metal welding. Its caloric power....kcal/kg places it among the first positions as compared to other gases increasing its welding capacity (Table one). Besides this fact , using an excess of hydrogen while welding has two great advantages;

- Hydrogen is the best reducer, making the eventuel oxides resulted from welding to be immediately reduced
- In the oxyhydrogen flame, due to its high temperature,the molecular hydrogen produced in excess dissociates into atomic hydrogen,absorbing thermic energy from the flame:

$$H_2 \rightarrow H+H \; - Q(Kcal) \qquad (1)$$

The atomic hydrogen recombines in molecular hydrogen when it is in contact with the welding seam and the base material ,both being colder than the hydrogen flame:

$$H+H \rightarrow H_2 + Q(Kcal) \qquad (2)$$

releasing a thermicenergy of dissociation which produces a local overheat with favourable effect upon the welding quality.The hydrogen welding is especially used nowadays at unsmeltable electrode welding of alloy steel which are handly smeltable. At this type of welding, the smelting energy is generated by the electric arc, the hydrogen rate being only that of oxide reducer and heat transfer from the arc central zone through atomic dissociation and subsequantly through molecular recombination(figure 1).

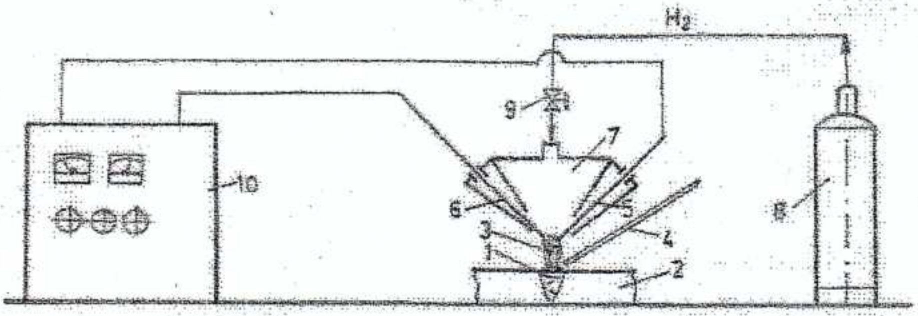

Fig. 1. The principle diagram of the electric-arc-welding achived by wolfram unsmeltable electrodes and hydrogen reducing gas.
1.welding seam; 2.base material;3. electric arc;4. weld material

Moreover hydrogen is also used in oxyhydrogen welding with oxygen and hydrogen cylinders, figure 2. The water and thermic energy resulted from the hydrogen combustion, lead to the welding of the weld material and the base one:

$$H_2 + 1/2/O_2 = H_2O + Q\ (\ldots \text{kcal}) \qquad (3)$$

Normally this type of welding should have already taken the place of the oxyacetylene welding resulted from carbide so far , because it is more profitable from the economic point of view. But things are different , due to two reasons. Firstly the hydrogen balance is closed in different industrial countries for the necessities in chemical industry of synthesis. Secondly the hydrogen storage in cylinders is economic only under presure of above 100 atmospheres.

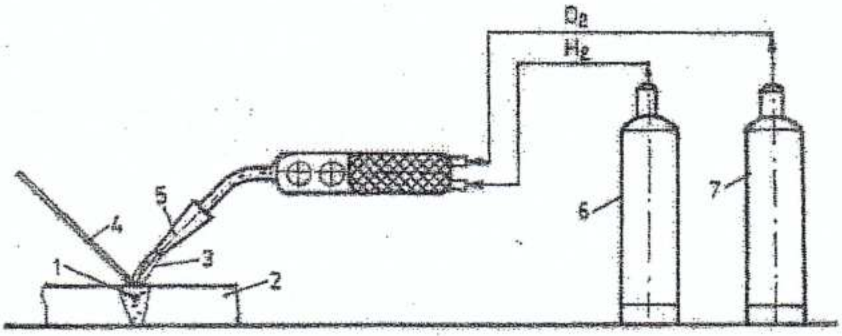

Fig. 2. The principle diagram of hydrogen flame welding
1-welding seam; 2-base material; 3.-oxyhydrogen flame; 4-weld material; 5-burner; 6-hydrogen cylinder; 7-oxygen cylinder

Under such high pressure , due to its reduced dimension, the hydrogen atom migrates through crystal lattice of cylinder walls leading to pressure loss.There are obviously solutions such as hydrogen transformation into balanced metal hydroxides in cylinder with molecular gaseous hydrogen while the gaseous hydrogen is consumed, its partial pressure lowers and the hydroxides decompose and complete the hydrogen.However, these solutions are rather expensive. Technics uses sporadically hydrogen flame welders in fine mechanics and jewelry manufacture. The hydrogen and oxygen necessary to produce smelting heat according to the reaction (3) are generated by electrolysis in accordance with the principle diagram from figure 3. The two gases, being collected inside composition in the superiour part of electrolytic tight-cell, are transferred by their own overpressure through a pipe to an alcohol separating switch for keeping the watery drops and vaporous apart from the gaseous composition and later on are ignited at burner in an oxyhydrogen flame.

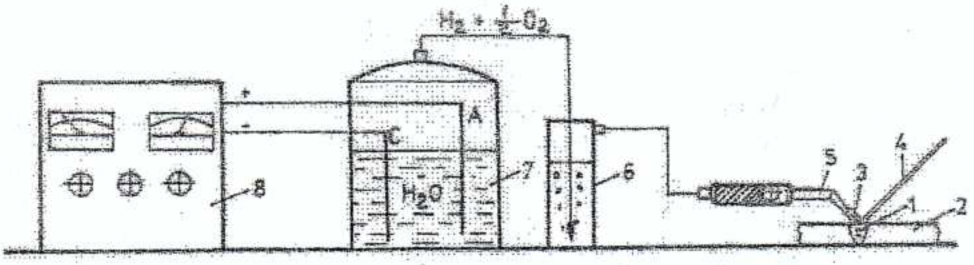

Fig. 3. The principle diagram of oxyhydrogen flame welding(hydrogen and oxygen being produced in stoechiometric relation) by water electrolysis.
1-welding seam; 2-base material; 3- oxyhydrogen flame; 4- weld material; 5- burner ; 6- ethyl alcohol barboter:; 7-electrolytic cell;8-current source for electrolysis

This type of welding with hydrogen and oxygen stoechiometric composition is the best from the energetic point of view , but it neither allows obtaining the reducing effect of flame nor that of thermal transmission through hydrogen atomic dissociation and later on its molecular recombination .It needs a hydrogen excess to get all these important advantages from welding . This excess is obtained by using a second cell of water electrolysis with hydrogen separating diaphragm, the oxygen resulted from this cell is blown out in the air.

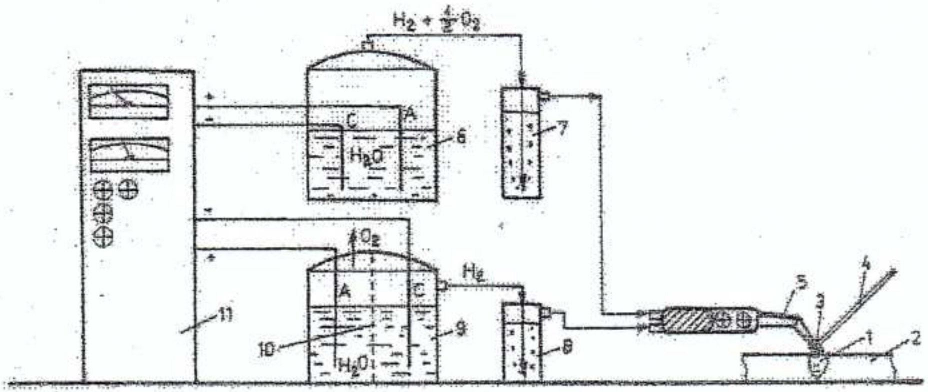

Fig. 4. The principle diagram of oxyhydrogen flame welding with reducing effect and thermal tramsmission by hydrogen excess(the hydrogen is used in unstoechiometric relation), all gases being obtained by water electrolysis
1-welding seam ; 2-base material ; 3-oxyhydrogen flame; 4-weld material; 5-burner; 6- electrolytic cell for producing the combustible composition ; 7, 8.-ethyl alcohol barboter;
9- electrolytic cell for hydrogen excess producing ; 10-separating diaphragm; 11-current source for electrolysis

Present day matter of water electrolysis

Nowadays the hydrogen necessary for economies of different countries is obtained from oil and more recently from coal and watery vapours. The hydrogen obtained from electrolysis is profitable only if there is cheap electric energy and in surplus during certain periods of time such as by night. In these circumstances the hydrogen is obtained and kept in underpressure containers and thus being a form of energy storage, being known the fact that electric energy cannot be stored. Figure 4 renders the principle diagram of an energetic structure based on hydrogen resulted from water electrolysis. In this diagram the electrochemical hydrogen welding has a well-defined place. One may talk about a world-wide energetic structure based mainly on hydrogen resulted from water electrolysis only when there are no material combustible gases, and oil reserves drastically diminish, being kept as raw-materials for the chemical industry . Another reason that might force a faster introduction of energetic structure based on electrolytic hydrogen is that of the excessive carbon-dioxide pollution of atmosphere, resulted from fossil combustible burning. Tenergetic structure should become at least as profitable as the actual one in order to replace the latter one. This fact has not been achieved yet, due mainly to the too low energy-yield of electrolysis. From a thermodynamic point of view the electrochemical water decomposition into hydrogen and oxygen requires a decomposition tension voltage of 1,23 V . This voltage is irrespective of electrolyte pH. When choosing the addition substances for electric conductivity increasing of water , one must take into consideration the fact that NaCl addition should be excluded because it leads to chlorine release at anode with high overtensions. The sulphates also lead to small conductivity increases and the acids cause advanced corrosion problems. For this reason the hydroxides which transform water into basic electrolyte are preferred to. Molar concentrations of 6-8 M are used . Nowadays specialsts work on water electrolysis of 80^0 C, terminal voltage of 1,8-2,0 V and electric current densities of 1-2,5 kA/m^2, energy expenditure of about 4 kW/h for a m^{3}N of hydrogen. The best for energy yield is represented by the relation between the electromotive force of combustion cells , being of about 0,8v, and terminal voltage of water electrolysis cells, being of about 1,8V. Keeping in mind the fact that the energy yield of both combustion cells and

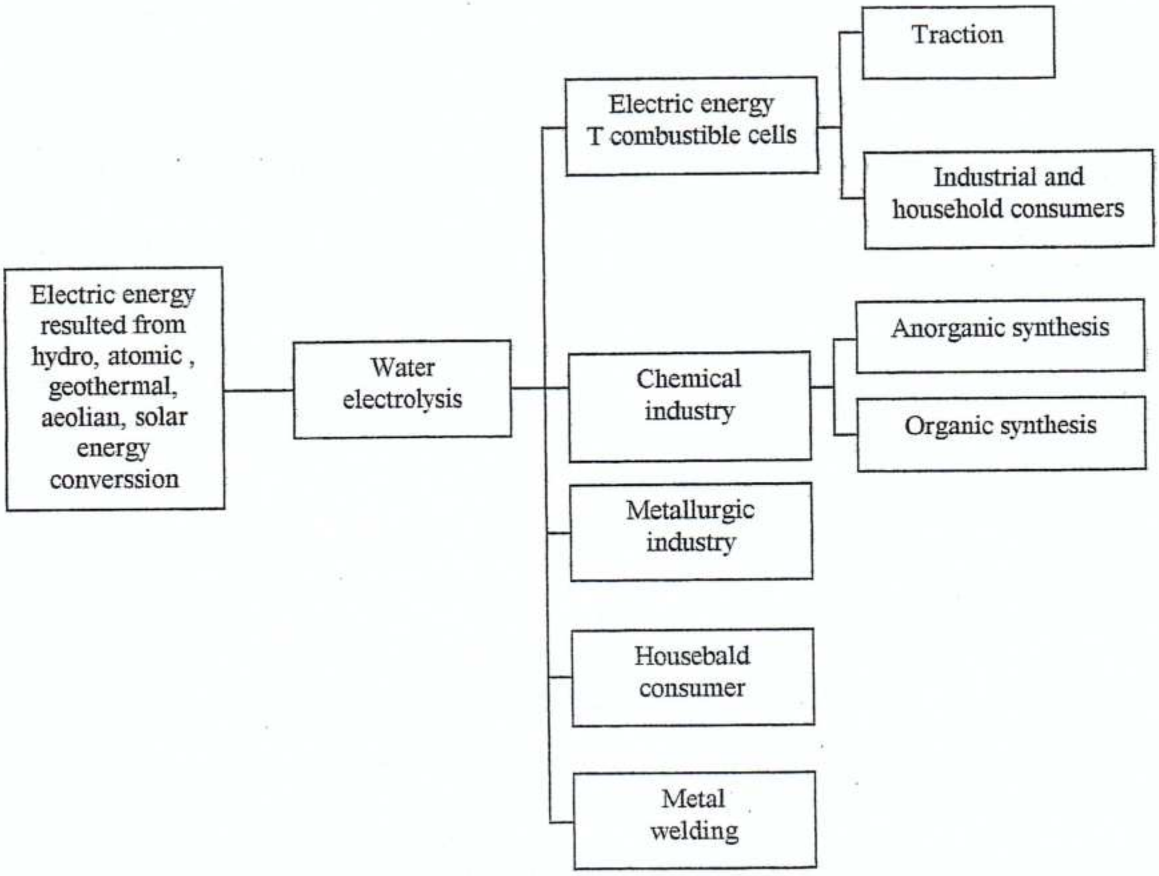

Fig. 5. Energetic structure based on hydrogen obtained from electrolysis and the hydrogen welding place in this structure

water electrolysis cells is near to 1, one can express the energy yield of conversion chain from figure 6 as being the following relation:

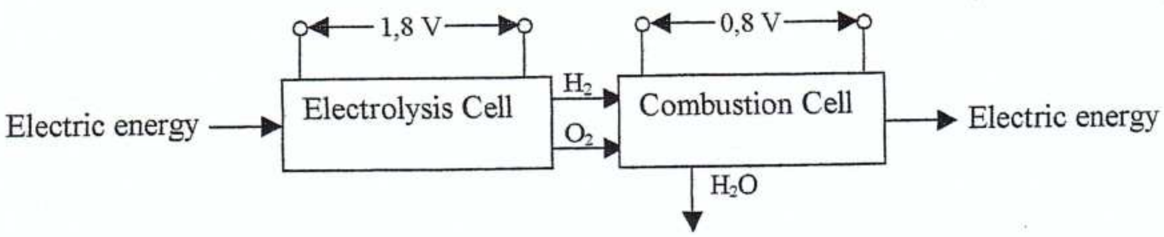

Fig. 6. Conversion chain : electric energy—>hydrogen + oxygen —>electric energy

$$\eta\text{energ}[\%]=\frac{\text{U combustion cell}|\text{Combustion cell t}}{\text{U electrolytic cell}|\text{Electrolytic cell t}}100=\text{U}\frac{\text{cell combustion}}{\text{cell electrolytis}}100\approx 45\%$$

where :

- η_{energ} – energy yield
- $U_{combustion\ cell}$ - electromotrive force of hydrogen and oxygen combustion cells
- $U_{electrolytic\ cell}$ - terminal voltage of water electrolysis cells
- $I_{combustion\ cell}$ - electric current by combustion cell
- $I_{electrolytic\ cell}$ - electric current by electrolysis cell
- T - electrolysis time

So the solution of increasing energy-yield is that of decreasing terminal voltage electrolytic cell in order to approach it to the theoretic tension of water electrolysis of 1,23 V, and if the conversion chain finishes with combustion cells, there are increasing measures of electromotrive force provided by the cell.

Mainly, the electrolytic tension decrease can be achieved by three measures and also by combinations between them.

1. Ohmic loss decrease in electrolytic cell
2. Overtension decrease by using new materials and structures for electrodes
3. Working voltage decrease by temperature increasing of the electrolyte

$$\frac{\partial\text{E desc}}{\partial\text{T}}\Big|_{\text{P}}\left(\text{H}_2\text{O liquid}\rightarrow\text{H}_2+\frac{1}{2}\text{O}_2\right)\approx-0{,}85\text{mV}/{}^0\text{K} \qquad (4)$$

where:

- ∂E desc = voltage variation of decomposition
- ∂T = temperature fluctuation of the electrolyte
- p = working pressure

When increasing temperature in order to decrease terminal voltage, one should take into consideration an optimal temperature related to the costs of temperature increasing and when the temperature is increased at 100^0C the electrolyte is to be found in its vapour state and pressure increasing leads also to terminal voltage increasing. The three above mentioned measures can also be combined, thus obtaining very notable electrolysis cells. Therefore, one can use special activated iron or nickel electrodes or nickel-zinc alloys electrodes. One can also improve the surface-active electrodes and can increase the working temperature from 80^0C to about 100^0C, fact that leads to decomposition tension decrease from 1,9V(80^{0}C) to a decomposition tension of about 1,7 V(100^{0}C) and current densities of 250kA/m^2.

Using the achievements of combustion cell technology refering to porous electrodes with high activity(such as platinum metals or nickel alloys-zinc on the hydrogen side and platinum metals on the oxygen side, having polymeric diaphragm with proton high conductivity as electrolyte), one can also achieve a sensitive decrease of water electrolysis voltage. At such cells, the demineralized water is introduced to anode, decomposing electrochemically into ½ O_2 and $2H^+$. The protons(hydrogen ions) pass through the diaphragm and are discharged at cathode. Laboratory experiments under temperature conditions of 80^{0}C, and current densities of 2,5 kA/m^2 generated an electrolysis voltage of only 1,55. Vapour electrolysis at 700-1000^{0}C , using porous catalytic deposited layers on a solid good conductor electrolyte for oxygen ions led to a decomposition voltage of only 1,2 V, to current densities of 1kA/m^2. On these terms, if the electromotrive force of hydrogen –oxygen combustion all of almost 0,9 V(possible value to be reached) as the last research show) is taken away, a total energy yield of about 75% is obtained according to relation (4), an energy yield which surpasses other conversion energy yields.

Conclusions

Using hydrogen-oxygen stoechiometric composition which is locally prepared in a special electrolytic cell, allows through its burning an oxyhydrogen flame obtaining of high temperature which can achieve local smeltings and metalweldings.The use of one more electrolytic cell, which separates the hydrogen from the oxygen, allows the hydrogen excess welding with reducing effect and thermal transmition. This welding technics promotion is related to water electrolysis matter, to the too small energy yield respectively, fact that leads to high costs. As the fossil combustible resources decrease, the research for alternative energetic sources increase. the interest of hydrogen for alternative energetic sources increases.The interest of hydrogen obtaining from water electrolysis is today bigger than ever . New materials and structures for electrodes, put into value by research concerning combustion cells, have already permitted sensible terminal volyage decreases of the electrolysis cell and by this, leading to energy yield increase.

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