DIFFUSIBLE HYDROGEN ON UNDERWATER WET WELDS PRODUCED WITH TUBULAR SHIELDED ELECTRODES USING INTERNAL GAS PROTECTION

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Abstract. *Shielded metal arc welding is considered the best process to be used in underwater steel structures. The main problem is diffusible hydrogen levels are high – up to 90ml/100gr of weld metal – when commercial rutile electrodes are used. These hydrogen levels cause, undoubtedly, cracks and pores, and in most cases lead to a low ductility of the weld metal in the tensile test. In underwater hyperbaric dry welding, Freon® was used as shielding gas in GMA Welding and a significant reduction of hydrogen levels was observed, indicating it could be a solution to the high hydrogen level produced by rutile electrodes. To evaluate this possibility in underwater wet welding, 4mm rutile tubular covered electrodes with a 3mm orifice were manufactured, and different gases (Ar, Ar-CO_2 and O_2) were added at continuous flow. Weld specimens were obtained using a gravity weld system, under 0.3m water pressure, and diffusible hydrogen contents were measured by gas chromatography. The O_2 addiction on arc welding atmosphere reduced significantly diffusible hydrogen levels on weld metal. Hydrogen content reduction due to O_2 introduction in the arc was associated with* predictable *reduction in the hydrogen availability on the molten poll and metallic drop. Beyond that, the creation of an oxidizing layer on the weld pool, which made hydrogen absorption difficult, as related by other authors, is the mechanism that guarantees oxidizing electrodes a lower content of diffusible hydrogen.*

Keywords*: Underwater Wet Welding, Diffusible Hydrogen, Tubular Shielded Electrodes, Gas Protection.*

1. INTRODUCTION

Underwater wet welding is most applicable in maintenance and repair of offshore oil platforms. Due to ambitious plans of raise in oil extraction on the Brazilian coast, especially on pre salt reservoirs, the development and creation of new technologies related to underwater welding are now in study. Several welding processes have been used in underwater welding. However, shielded metal arc welding (SMAW) is the most used process due to a number of factors, such as: relative low cost, flexibility and versatility.

Nevertheless, underwater wet welding has several problems, for example, hydrogen cracks, porosity, loss of alloying elements, non-metallic inclusions formation and arc instability. Hydrogen cracks are probably the most critical problem, being responsible for a significant reduction on mechanical properties of the welded joint. It is not very well known the mechanism of formation of hydrogen cracks. It is known that the related cracks occurs under four factors: presence of diffusible hydrogen in high content on the weld metal and heat-affected zone, presence of tractive tension on the weld joint, susceptible microstructure and temperatures lower than 200°C. Cold cracking on underwater wet welding is a dramatic problem since water from the environment may disassociate in the electric arc, supplying H+ ions for the molten weld pool, leading to a substantial raise of the diffusible hydrogen content on the weld metal. Besides, the presence of water leads to a significant raise of the cooling rate of weld metal and heat affected zone (HAZ), and, consequently to the formation of a more fragile microstructure, propitiating the formation of cold cracks. To eliminate hydrogen cracks one of the four factors described above has to be eliminated. However, such thing is not so simple. The development of new hybrid consumables (oxi-rutilic) and the use of appropriate techniques, during and after the welding have boosted researches in this area.

Electrodes most used in underwater wet welding are rutilic and oxidizing. Rutilic electrodes have good arc stability and weld metal with significant tenacity and ductility. On the other hand, high hydrogen content on the weld metal becomes a depreciable factor in its use. Oxidizing electrodes produce weld beads with lower hydrogen content with the disadvantage of loss of alloy elements and poor weldability. The possibility of reduce the hydrogen level of rutilic electrodes, may be a reasonable alternative on underwater weld welding, since it can bring together the advantages of oxidizing and rutilic electrodes. To create an oxidizing layer on the weld pool, shielding gas from an outside source can be used, similarly to GTA and GMA welding. In this paper, rutilic electrodes with shielding gas were used in order to obtain a welding process with the operational characteristics of a rutilic electrode and lower hydrogen content, as found with oxidizing electrodes. Several shielded gases were tested to figure out which one is the most efficient in reducing hydrogen level content on weld metal.

2. LITERATURE REVIEW

Underwater wet welding has been object of study of several researchers. The process applied to underwater wet welding has several aspects that make it different from conventional welding processes, such as: higher difficulty of open and maintain the electric arc, less visibility for the welder, and higher levels of insalubrity and periculosity. The aquatic environment causes several problems, for example: porosity, cold cracking (hydrogen cracks), solidification cracks, less stable electric arc, loss of alloying elements (deoxidizers), etc.,(Filho et al, 2003), what can lead to loss of mechanical properties of the submerged welded joints compared to the same properties of joints welded in atmospheric conditions. Figure 1 shows the effect of the aqueous environment on mechanical properties of underwater wet welded joints.

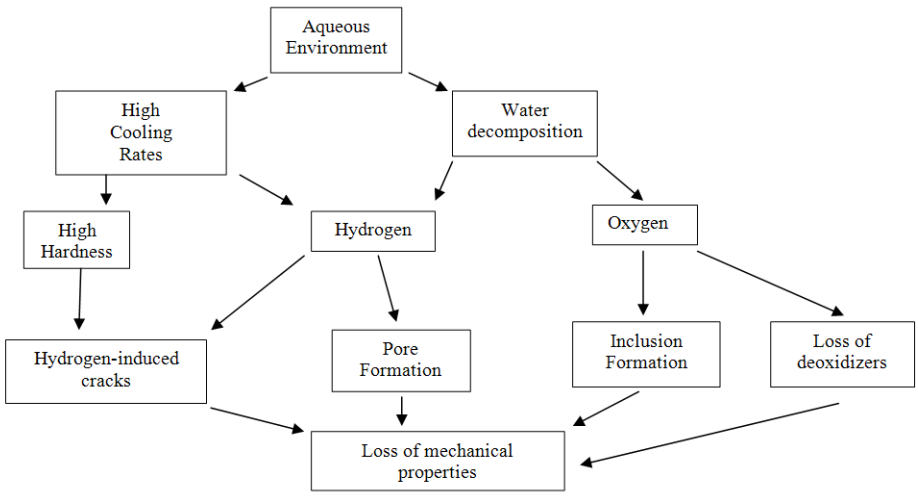


Figure 1. Effect of the aqueous environment on mechanical properties of underwater wet welded joints (Pope, 1995)

Among those discontinuities mentioned above, cold cracking and porosity are the most concerning metallurgical factors related to underwater wet welding. Welding porosity is affected by water depth, type of electrode and arc stability (Liu *et al*, 1994). Pessoa (2007) reported that the porosity of wet welds is proportional to depth. However, the occurrence of pores in the wet weld metal was not observed in depth lower than 5 meters (Suga e Hasuí, 1986). The insertion of a shielded gas may influence on porosity of wet weld metal, but as in this paper the welds were made at 0.3m depth, it was not possible to verify the influence of a protection gas on porosity of wet weld metal.

The hydrogen cracks are caused by four factors (Rowe and Liu, 2001):

- Diffusible hydrogen levels;
- High stresses;
- Susceptible microstructure (martensite);
- Low temperatures (between -100 to 200ºC).

Hydrogen on the weld metal and heat-affected zone may happen by different reasons, such as humidity and oil on the surface of weld metal or electrode, decomposition of cellulose and humidity on the shielding gas. High stresses may occur due to contraction of weld metal during solidification and thermal cycles during welding on situations where there is restriction of movement of weld joints. In underwater wet welding, high cooling rates are observed, leading to an increase of martensite formation and, consequently, susceptibility to hydrogen cracking on HAZ. These consequences can be avoided by using weld metal with equivalent carbon content lower than 0.40% (Liu *et al*, 1994). Equation (1) shows how equivalent carbon is calculated. Additionally, it is important to notice that most of underwater wet welding applications are carried out in temperatures between -100°C and 200°C (Bailey et al, 1993). This way, those described conditions related to formation of hydrogen cracking are met in underwater wet welding.

$$CE=C+Mn/6+ (Cr+Mo+V)/5+(Ni+Cu)/15 \qquad \text{Eq. 1}$$

The mechanism that leads to hydrogen cracking is not very well known (Kou, 2003), even though many theories have been purposed. Troiano (1960) related that hydrogen promotes crack growth by reducing cohesive forces of the material. Petch (1952) purposed that hydrogen promotes crack growth by reduction of the superficial energy of the crack. Beachem (1972) related that hydrogen promotes microscopical deformation on the tip of the crack. Savage *et al.* (1976) explained hydrogen cracking on weld metal based on Troiano's theory. Gedeon and Eagar (1990) reported that

their results fundamented and expanded Beachem's theory. Figure 2 shows the aspect of hydrogen cracks on HAZ in two different situations.

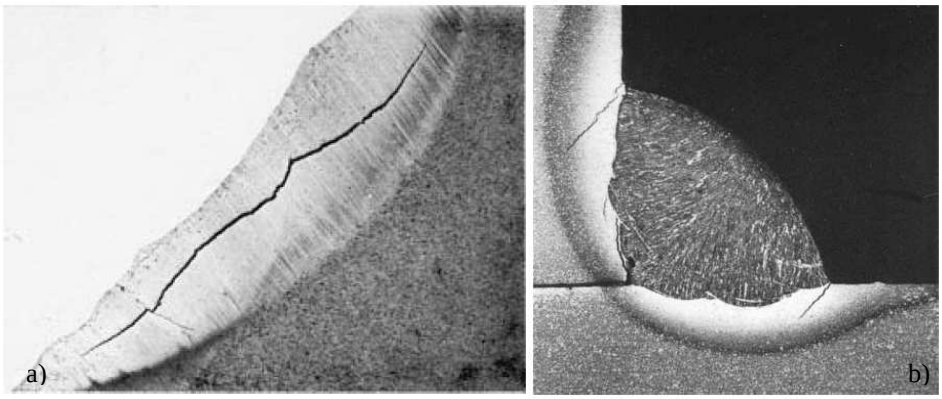


Figure 2. a) Under bead cracks on HAZ in low alloy steel. 8x Mag. (Bailey, 1981), b) Cold cracking in a weld bead using as base metal 1040 steel with 4.5x Mag. (Kou, 2003)

Several methods were developed to measure hydrogen content on weld metal. Methods most commonly used are: mercury and gas chromatography. In this second method, a weld sample is transferred to a chamber and it is heated to 45°C for 72 hours, in order to accelerate hydrogen diffusion through the weld metal. After the 72 hours, the sampler is connected to a chromatographer (equipment that measures hydrogen content in the sampler). In this method, other gases are isolated, and only hydrogen content is measured. On the other hand, high cost of the equipment can become an impeditive factor about this method (Kou, 2003).

The effect of shielding gases on GMA and FCA welding was studied by Mirza and Gee (1999). They reported lower diffusible hydrogen levels when CO_2 was used as shielding gas. According to Mirza and Gee (1999), carbon dioxide also affects penetration of the weld bead. A mix of CO_2 and Argon as shielding gas is responsible for dislocation of hydrogen from the areas with higher temperatures of the electric arc, areas of higher absorption of hydrogen, reducing the total amount of hydrogen on the weld pool. Table 1 shows results obtained by Mirza and Geee (1999) related to effect of shielding gas on diffusible hydrogen on GMA and FCA welding.

Table 1. Effect of shielding gas on diffusible hydrogen content.

Diffusible Hydrogen, ml/100g					
	Air	Air-5%CO_2	Air-20%CO_2	CO_2	Air-2%O_2
Solid Wire					
Test 1	1.86	1.51	1.32	0.78	1.88
Test 2	1.88	1.61	1.26	0.84	2.31
Test 3	2.00	1.32	1.36	0.91	1.93
Test 4	1.67	1.58	1.21	0.88	1.91
Average	1.85	1.51	1.29	0.85	2.01
Standard Deviation	0.12	0.11	0.06	0.05	0.18
Metal Cored					
Test 1	8.93	8.12	5.67	3.86	10.21
Test 2	9.02	8.71	5.69	3.91	8.86
Test 3	9.32	9.32	5.86	3.80	9.31
Test 4	10.62	9.11	5.58	3.23	8.99
Average	9.47	8.82	5.70	3.70	9.34
Standard Deviation	0.68	0.46	0.17	0.27	0.53

Chandiramani (1994) reported the use of Freon-12 on GMA Welding, using CO_2 as shielding gas. The author concluded that Freon-12 addition to CO_2 in GMA Welding generated a significant reduction of hydrogen content, in the air and water environment. Hydrogen content reduction was dependent to Freon-12 additions. 0.5 l/min of Freon-12 mixed with 18 l/min of CO_2 was enough to reduce hydrogen levels in welds from 6 ml/100g of weld metal to 1.8 ml/100g. On wet welding, it was reported that 4 l/min of Freon-12 mixed with 15 l/min of CO_2 was responsible of a

reduction of hydrogen content from 30ml/100g to 10 ml/100g. Results obtained by Chandiramani (1994) related to diffusible hydrogen content reduction can be seen in Tab. 2.

Table 2. Effect on diffusible hydrogen with Freon-12 additions (Chandiramani, 1994)

No.	Wire Dia. (mm)	Wire Feed (m/min)	DCV (volts)	Medium	Average Hydrogen Content (mL/100g)	Remarks
1	0.8	8	32	Air	1.8	18 L/min CO2 + 0.5 L/min Freon-12
2	0.8	7	50	Fresh water	31.5	18 L/min CO2 + 0.5 L/min Freon-12
3	0.8	7	50	Fresh water	25.9	18 L/min CO2 + 1.0 L/min Freon-12
4	0.8	7	50	Fresh water	21.9	16 L/min CO2 + 3.0 L/min Freon-12
5	0.8	7	50	Fresh water	11.6	15 L/min CO2 + 4.0 L/min Freon-12
6	0.8	4	32	Fresh water	9.0	15 L/min CO2 + 4.0 L/min Freon-12
7	0.8	5	32	Fresh water	9.8	15 L/min CO2 + 4.0 L/min Freon-12
8	0.8	6	32	Fresh water	11.6	15 L/min CO2 + 4.0 L/min Freon-12
9	0.8	7	32	Fresh water	8.3	15 L/min CO2 + 4.0 L/min Freon-12

Pessoa *et al* (2007) studied the effect of exothermical and oxidizing additions in tubular electrodes (similar to the electrodes used in this work) on underwater wet welding in order to reduce porosity of weld metal through chemical reactions on arc atmosphere and weld pool, reducing gases transferred to the weld pool through molten metal on the tip of the electrode. After the addition of CaC_2 and Al on internal flux of the electrode, chemical composition and porosity were analyzed. Aluminum addition promoted exothermical reactions with O_2, attenuating its effect on pore formation. Additionally, those reactions could also increase welding energy and cooling rate between temperatures from 800 to 500ºC. CaC_2 addition protected droplets from oxidizing reactions during growth and detachment from the tip of the electrode. Pessoa *et al* (2007) observed a significant porosity reduction, an increase of carbon content and changes on microstructure of weld metal and a substantial increase of acicular ferrite on weld metal with additions of CaC_2 and Al. These two elements were also responsible for Mn and Si preservation. Figure 3 shows that CaC_2 and Al additions were efficient in porosity reduction on weld metal.

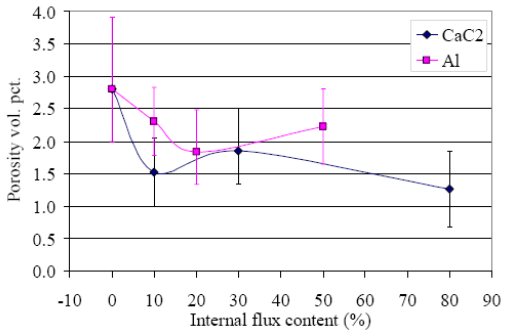


Figure 3. Effect of CaC_2 addition on porosity reduction (Pessoa et al, 2007)

The addition of internal shielding gases may also affect morphology of the weld bead. As reported (Mill, 1990; Kou and Limmaneevichitr, 2000), small additions of active elements, such as sulfur and oxygen, considerably modify surface tension of iron γ and other metals. Heiple and Roper (1982) reported that surface tension gradients and Lorentz force are the main forces that interact in order to promote flow of fluid metal on the weld pool, and, consequently, determining weld bead morphology. Concentration of active elements on the weld pool, such as S, Se and O, affects the angular coefficient of dγ/dT curve. Literature reports that dγ/dT is positive for oxygen concentration higher than 40 ppm (Keene, 1988). Since molten metal flow is from lower to higher surface tensions, flow on weld pool is radial to the outside, with active elements in high concentrations. This affect added to Lorentz forces will result in a weld bead with higher penetration. Lack of active elements, which can be caused by reaction with elements such as Al, Si and Ca, will generate a surface tension gradient in the opposite direction of Lorentz force. Since thermocapilarity force (Marangoni Convection) is more influential than Lorentz force, the weld bead produced will have lower penetration.

This study has the intention to investigate the effect of different shielding gases on diffusible hydrogen content on weld metal, in SMA welding using tubular electrodes. Since Pessoa (2007) observed that CaC_2 and Al additions modified chemical composition and porosity of weld metal, it is reasonable to assume that the same electrode with a shielding gas through its inside (without internal flux) will affect several aspects of the weld bead. It was concluded that an insertion of a shielding gas through the tubular electrode affected diffusible hydrogen content on weld metal and

weld bead morphology. Likewise, morphology and hardness of heat affected zone (HAZ) and weld metal were also observed and no significant changes were found.

3. MATERIALS AND EXPERIMENTAL METHODS

In this work, rutilic tubular electrodes were used and its fabrication was the same as commonly used in tubular electrodes for FCA welding. Electrodes were taken to an extruding machine so that external rutilic flux could be added, resulting in the rutilic tubular electrode. The electrode has the following dimensions: core rod with 4.0 of outside diameter, internal hollow with 2.0 mm of diameter and 0.9 mm coating thickness. The electrodes were waterproofed with a layer of varnish. Figure 4.a shows some electrodes used in the experiment. Figure 4.b shows the cross section of the electrode. It was used a low carbon plate as base metal.

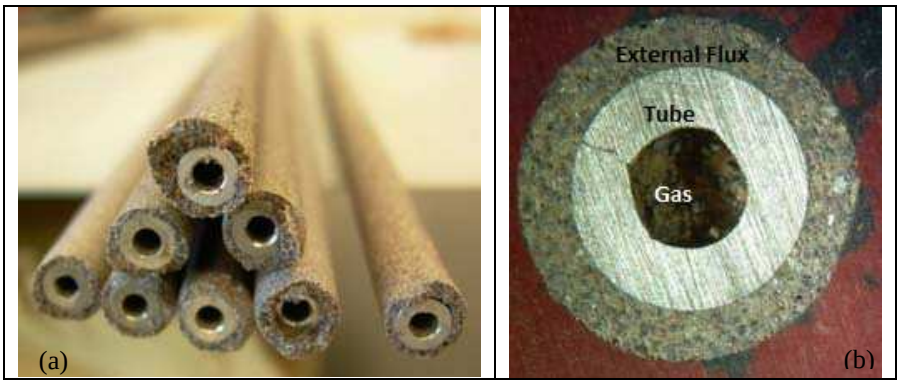


Figure 4. a) Tubular electrodes and, b) Cross section of a tubular electrode

Hydrogen content measurements were made accordingly to AWS D3.6M using gas chromatography. For each shielding gas, including a condition where no gas was used, at least four tests were done. Shielding gases used were: Argon, Argon-CO_2 (18%) and O_2. Weld beads were carried out using a gravity system as shown in Fig. 5. Welding parameters used are showed in Tab. 3. The mass flow was chosen for the best condition welding for each shielding gas. Polarity used was DCEN with an electric power source welding machine.

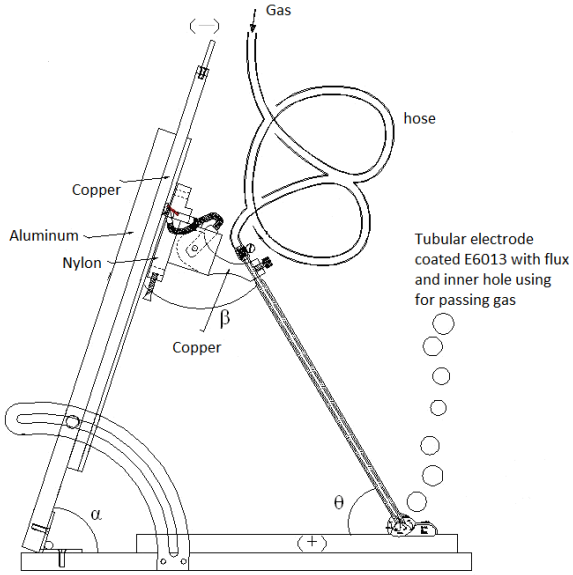


Figure 5. Scheme of Gravity feeding system used in the experiment

Table 3. Welding parameters applied in the experiments.

Shielding Gas	Polarity	Current(A)	Flow (l/min)	Θ	α
Without gas	DCEN	100	0	55º	90º
Argon	DCEN	100	2.25	60º	90º
Argon- CO_2 (18%)	DCEN	100	2.34	60º	90º
O_2	DCEN	100	1.82	60º	90º

For weld bead characterization, macrographs were made for each condition. The weld beads were sectioned at the beginning, middle and end for morphology analysis. The samples were prepared following standard metallographic procedures and etched with a 5% Nital solution and then photographed. Finally, the morphology was quantified using Quantikov (Pinto, 1996), where depth and width of the weld bead were quantified. A representative micrography for each welding condition was made, using a 2% Nital solution, in order to verify if the insertion of a shielding gas inside the tubular electrode would affect the microstructure and hardness of weld metal and heat affected zone.

During welding, voltage and current values were acquired at 1 kHz. Mean voltage and number of short circuits were calculated. Short circuit was considered every time when voltage value found was fewer than five Volts. Finally, S parameter of voltage was also calculated, and it is defined as the quotient between the higher and the lower arc voltage value in a time interval. S parameter close to 1 indicates a more stable electric arc.

Vickers Hardness measurements was performed on weld metal and Heat Affected Zone (HAZ). Three measurements were made for each condition as shown in Fig. 6. The load used was 2,9N during 25 seconds.

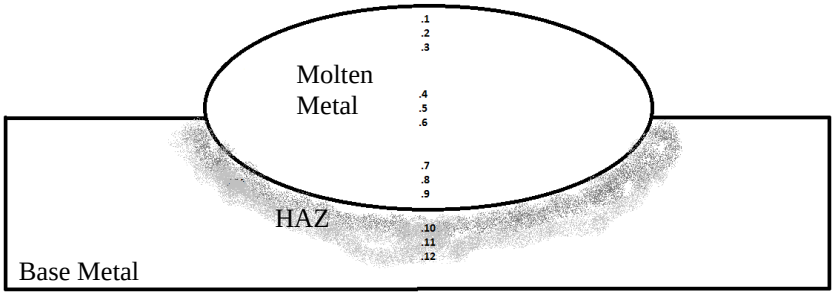


Figure 6. Schematic figure showing where Vickers Hardness test was performed on weld metal and HAZ

4. EXPERIMENTAL RESULTS AND DISCUSSION

The surface appearance analysis of the weld beads was made. The best result was obtained for the condition in which was not used shielding gas with reasonable surface appearance. The worst result was obtained using oxygen gas. In general, the surface appearance of the weld beads was not good when a shielding gas was used. It is possible that the insertion of the shielding gas is leading to instability during metal transfer, which may have resulted in a more erratic weld bead when argon, argon- CO_2 (18%) and O_2 were used. The Figure 7 shows the weld beads made with different shielding gases and without gas protection.

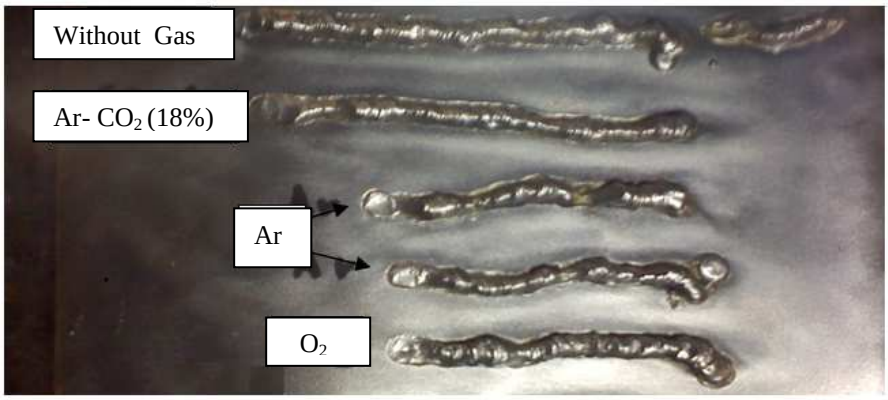


Figure 7. Bead on plate for different welding conditions

The insertion of the shielding gas was harmful to the operability. The presence of the shielding gas increased considerably the length of the cone at electrode tip. Welds were made by a welding gravity system and the welding is carried out primarily by the drag of the tip of the electrode on the plate. So, it is not possible to control directly the length of the electrode cone. Thus, it was found some difficulties to perform wet welds using shielding gas, because the arc breaked off often on undesirable points due to excessive cone length.

Concerning the analysis of signals, it was observed that the shielding gas increased the average voltage of welding, as shown in Table 4. A high welding voltage value can not be attractive to the diffusible hydrogen of the weld metal, because, in these cases, with high welding voltage, the metallic drop stays a little longer exposed to the atmosphere of the arc, which can facilitate abortion of hydrogen to the metallic drop. However, as can be seen below in this paper, this was not the predominant factor in the outcome of diffusible hydrogen for the various cases analyzed. With regard to the occurrence of short circuits, it was observed only in the condition without shielding gas. Finally, the arc stability parameter (S) remained stable (close to 1) when the three gases were used and increased when welding without shielding gas. This result is due to the greater number of short circuits in the condition of welding without shielding gas. The insertion of a shielding gas during welding in coated tubular electrode and the appropriate changes in parameters of voltage, stability and number of short circuits must be better understood. It is possible that the arc atmosphere is getting hotter with the presence of shielding gas and thereby increasing the consumption of the core rod in relation to the metallic coating, resulting in a higher cone length, higher voltage, lower number of short circuits and higher arc stability (S).

Table 4. Voltage and number of short circuits

	Voltage(V)	S	NSC
Without gas	27.5	1.73	104
Argon	38.7	1.15	0
Argon-CO_2(18%)	38.5	1.17	0
O_2	39.9	1.17	0

The insertion of a shielding gas increased the ratio D / W (Depth / Width), being more pronounced when oxygen gas was used. This result may be due to the marangoni convection, as previously reported, the oxygen has an active role in the weld pool convection, which can change the surface tension profile and, therefore, creating a general convective flow from the edge to the center of the weld, resulting in a weld bead with smaller width and greater depth and ratio D/ W. The same effect may be occurring with the mixture Ar-CO_2, however, in a less intensity than with oxygen. The results of measurements of the weld bead geometry (D / W (Depth / Width)) are shown in Figure 8.

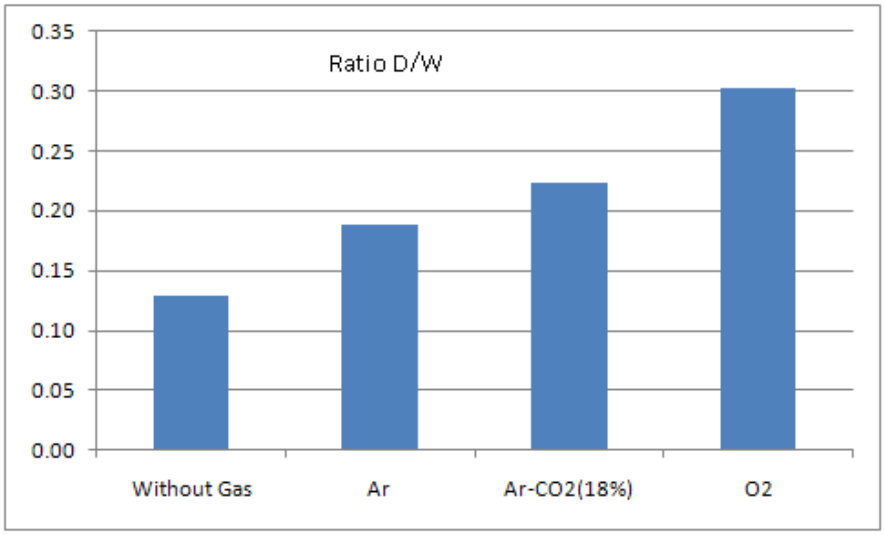


Figure 8. Weld bead geometry

No meaningful changes was found on microstructure and hardness in the four welding conditions, i.e., with shielding gas (Argon, Argon-CO_2 (18%) and O_2) and without shielding gas. Thus, the insertion of the shielding gas on the tubular shielded electrode did not affect the cooling rate of the weld metal and, consequently, the weld metal hardness and microstructure. Figures 9 and 10 are summarized the results of Vickers hardness and microstructure, respectively.

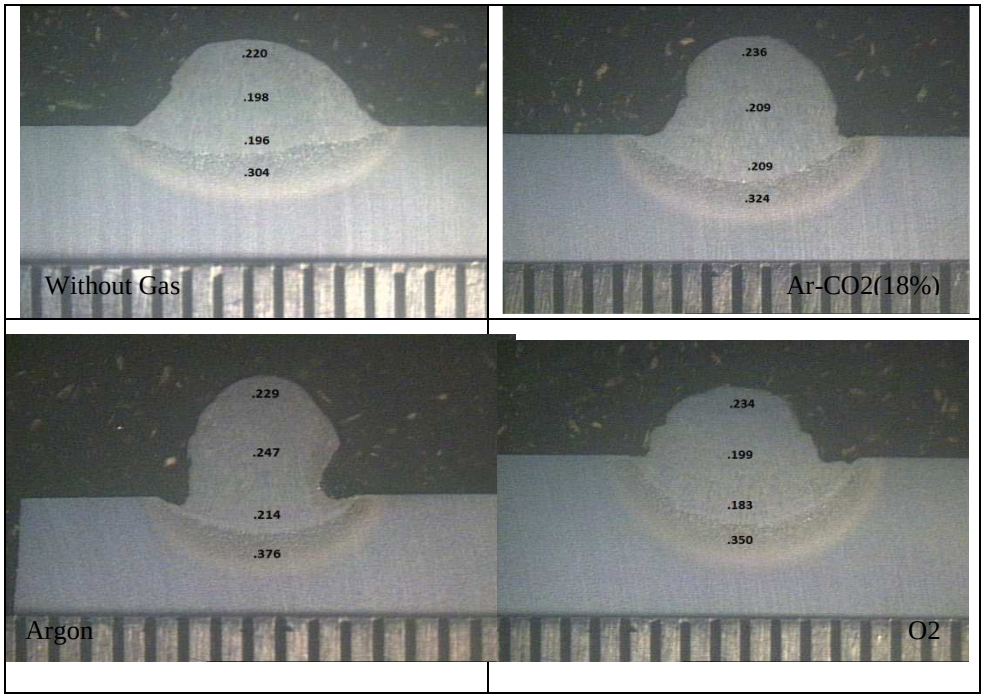
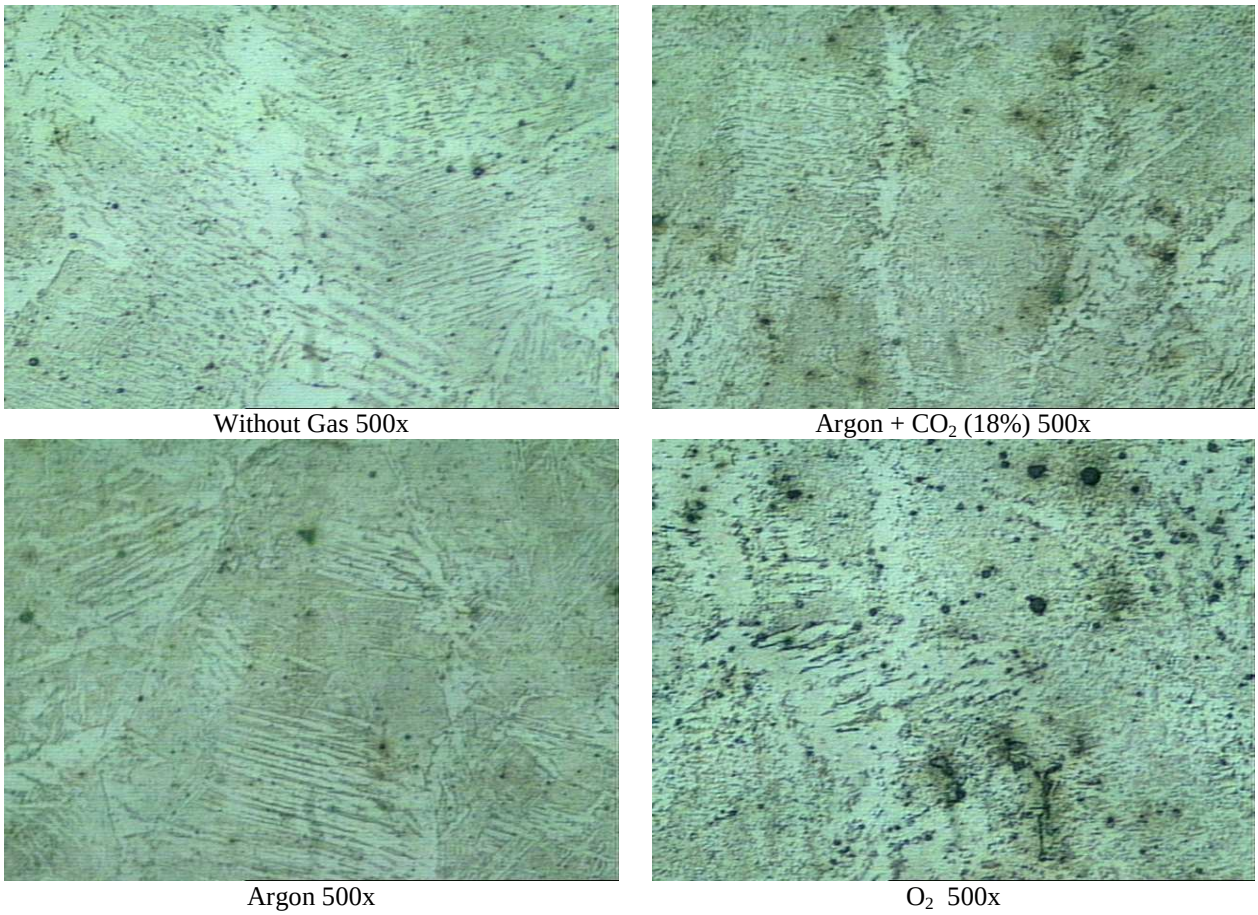


Figure 9. Weld bead macrograph and its hardness



Without Gas 500x

Argon + CO_2 (18%) 500x

Argon 500x

O_2 500x

Figure 10. Representative micrographies of the weld metal for different welding conditions (500x magnification)

The results of diffusible hydrogen in weld metal can be seen in Figure 11.b. O_2 insertion has reduced the diffusible hydrogen significantly. The diffusible hydrogen measured in welds made without shielding gas was around 42.6 ml/100g while welding with oxygen, the hydrogen diffusible found reduced to 22.9 ml/100g. The use of argon and argon- CO_2 mixture (18%) was not effective in reducing the diffusible hydrogen. The understanding of the thermodynamics of the reaction of hydrogen and oxygen in liquid metal (molten droplet and weld pool) may be useful to explain the relationship between the lowest diffusible hydrogen in weld metal. In the Elliot diagram [Medeiros (1997) apud Elliot et al (1963)], the equilibrium hydrogen-oxygen occurs in an inverse relationship, so, as the partial pressure of oxygen increases in the arc atmosphere, the amount of available hydrogen tends to reduce. It was expected that with CO_2 shielding gas would have the same effect of oxygen on the reduction of diffusible hydrogen. However, expectations were not achieved, since the diffusible hydrogen using CO_2 was close to the values obtained with argon gas and without gaseous protection. As was used a mixture of Ar- CO_2 (18%), it is suspected that the amount of CO_2 was insufficient to reduce the diffusible hydrogen. The gas argon did not change significantly the diffusible hydrogen, as can be seen on the Figure 11.b. On Figure 11.a (Medeiros, 1997 apud Elliot, 1963) is shown in the diagram of equilibrium hydrogen-oxygen at 1600 º C, and Figure 11.b, we can graphically see the influence of shielding gas on diffusible hydrogen in weld metal.

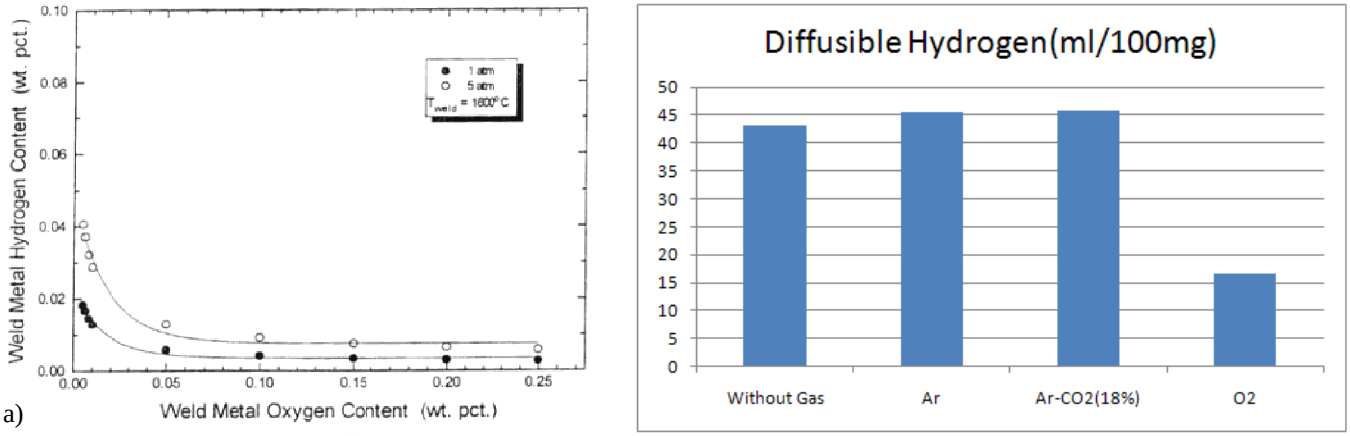


Figure 11. a) Hydrogen-oxygen equilibrium at 1600ºC (Medeiros, 1997 apud Elliot, 1963) and, b) Diffusible hydrogen for different welding conditions [Without gas, Argon, Ar- CO_2 (18%), O2]

5. CONCLUSIONS

Based on the results of this study the conclusions are as follows:

1. The addition of oxygen as shielding gas was effective in reducing the diffusible hydrogen from wet welds. The diffusible hydrogen was reduced from 43 ml/100mg for the condition without shielding gas for 16 ml/100mg using oxygen as shielding gas. For other shielding gas used (argon, argon-CO2 (18%)), the results of diffusible hydrogen were similar to those obtained in the condition without shielding gas;
2. The addition of the shielding gas did not significantly alter the microstructure of the weld metal;
3. There was no significant change in hardness of weld metal and heat affected zone with insertion of a protective gas;
4. Regarding the surface appearance of weld beads made, the best results were obtained without using shielding gas, looking very reasonable. The worst aspect weld surface was obtained using oxygen. It is likely that the use of a shielding gas is influencing the metal transfer and therefore the surface appearance of the weld bead;
5. Wet welds made with oxygen presented higher penetration. The Marangoni effect can be the cause of this result, as discussed above;
6. In all conditions tested, the insertion of the shielding gas has increased the arc instability.

6. ACKNOWLEDGEMENTS

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