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Effect of the welding environment and storage time of electrodes on the diffusible hydrogen content in deposited metal

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ABSTRACT: In the study the glycerin displacement method was used for determination of diffusible hydrogen content in deposited metal. Specimens were welded in the air and in the water with covered rutile electrodes. The first part of the specimens was made immediately after opening the package of the electrodes. The electrodes were then stored in opened packages in laboratory conditions that allowed for contact with the air for three years. After that time, the second part of the samples was made. The results of the measurements of the diffusible hydrogen amount in deposited metal ranged from 32.61 to 39.95 ml/100 g for specimens welded in the air and from 51.50 to 61.34 ml/100 g for specimens made in the water. The statistical analyses were performed in a Statistical software package using the ANOVA module (one-way analysis of variance) with an assumed significance level $\alpha = 0.05$. The assumption of normality was verified by the Shapiro-Wilk test. The homogeneity of variance was verified by the Levene test. In the next step, post-hoc analyzes were made. The aim was to determine which averages are significantly different. Scheffe, Tukey, NIR Fisher, Newman-Keuls and Duncan tests were used. Possible changes in the diffusible hydrogen content in deposited metal resulting from storage time of electrodes (3 years) were verified by Student's t-test. All of the statistical analysis shows that the storage time of the electrodes has no significant influence on the diffusible hydrogen content in deposited metal regardless of the welding environment.

KEYWORDS: Covered electrodes; Diffusible hydrogen; Glycerin method; Underwater welding; Weldability; Wet welding

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RESUMEN: *Efecto del sistema de apantallamiento de la soldadura y el tiempo de almacenaje de los electrodos en el contenido de hidrógeno difundido en el metal depositado.* El método de desplazamiento de la glicerina se utilizó para determinar el contenido de hidrógeno difundido en el metal depositado. Las muestras se soldaron en aire y en agua con electrodos recubiertos de rutilo. En la primera parte, las se soldaron inmediatamente después de abrir el paquete con los electrodos. Posteriormente, los electrodos se almacenaron en paquetes abiertos en el ambiente de laboratorio durante 3 años. Pasado este tiempo, se realizó la segunda parte de las muestras. Los resultados de las mediciones de la cantidad de hidrógeno difundido en el metal depositado varió de 32,61 a 39,95 ml/100 g para muestras soldadas al aire y de 51,50 a 61,34 ml/100 g para muestras soldadas en agua. Los análisis estadísticos se realizaron utilizando el software Statistica, módulo ANOVA (análisis de varianza de una vía) con un supuesto nivel de validez α=0,05. La normalidad fue verificada por el ensayo Shapiro-Wilk. La homogeneidad de la varianza se verificó mediante el ensayo Levene. En la etapa siguiente, se realizaron análisis post-hoc. El objetivo fue determinar si los promedios son significativamente diferentes. Se utilizaron los ensayos Scheffe, Tukey, NIR Fisher, Newman-Keuls y Duncan. Los posibles cambios en el contenido de hidrógeno difundido en el metal depositado, resultante del tiempo de almacenamiento de los electrodos, se determinaron mediante el ensayo "t" de Student. Los resultados del análisis estadístico muestran que el tiempo de almacenamiento de los electrodos no tiene una influencia significativa en el contenido de hidrógeno difundido en el metal depositado, independientemente del sistema de apantallamiento utilizado en la soldadura.

PALABRAS CLAVE: Electrodos recubiertos; Hidrógeno difundido; Método de la glicerina; Soldabilidad; Soldadura en húmedo; Soldadura sumergida en agua;

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1. INTRODUCTION

Welding in underwater environment is most often applied as a method of repairs water constructions. The process is most often carried out with direct contact with water (wet welding) with the use of covered electrodes (Fydrych *et al.*, 2015; Wang *et al.*, 2018). Water environment intensifies some problems that have a negative impact on weldability of steel, such as a rapid cooling rate (Guo *et al.*, 2017; Tomków *et al.*, 2018a; Sajek, 2019) and the presence of residual stresses (Aloraier *et al.*, 2004; Hu *et al.*, 2017; Han *et al.*, 2019; Wang *et al.*, 2019a; Wang *et al.*, 2019b). The environment also has an impact by increasing the diffusible hydrogen content (Fydrych and Łabanowski, 2015; Chen *et al.*, 2018). The water is a source of potential hydrogen and diffusible hydrogen content in deposited metal depends on this amount. Hydrogen could be a source of corrosion (Świerczyńska *et al.*, 2017a), and it is also a factor that is responsible for cracking (Yadav *et al.*, 2017; Pascual-Guillamón *et al.*, 2018), especially cold cracking, which is the biggest problem in underwater welding (Guo *et al.*, 2015; Tomków *et al.*, 2018b). Also, the hydrogen has a big influence on the mechanical properties of welded joints (Pandey *et al.*, 2017a; Pandey *et al.*, 2017b).

The diffusible hydrogen content in deposited metal depends on welding conditions such as the filler and the base material surface condition. It also depends on other parameters including the arc voltage, travel speed, welding current and polarity and stick out length (Fydrych and Łabanowski, 2015; Schaupp *et al.*, 2017; Schaupp *et al.*, 2018).

Hydrogen measurements are standardized (ISO 3690 (2012)). Literature recommended the use of the mercury method for hydrogen measurements (Padhy *et al.*, 2015a; Padhy *et al.*, 2015b). The most important disadvantage of the mercury method is the toxicity of mercury (López *et al.*, 2014; López *et al.*, 2015). The measurement error resulting from the solubility of hydrogen in glycerine is less important in the case of testing of high-hydrogen processes, for example: welding with rutile or cellulose electrodes, or welding in water environment (Świerczyńska *et al.*, 2017b). As usage of the mercury is prohibited, one of the most prospective methods of low-temperature measurement of hydrogen content is glycerine method. Disadvantages of the results glycerin method in comparison with the mercury method are more difficulty in repeating the results and lower measurement accuracy. To compare results between these two methods, it is necessary to use of relatable data points (Fydrych and Łabanowski, 2015). However, the capability of recalculating the results is limited to 35 ml/100 g of diffusible hydrogen in deposited metal, so it cannot be used in underwater welding. Recent research showed that results up to 80 ml/100 g can be recalculated according to the following formula (Fydrych and Łabanowski, 2015):

$$HDme = 1.21 \times HDgl + 2.60 \quad (1)$$

Where HDme-hydrogen content in deposited metal determined with mercury method (ml/100 g) and HDgl-hydrogen content in deposited metal determined with glycerin method (ml/100 g).

The aim of the undertaken studies was to determine a relationship between the storage time of the electrodes and the amount of diffusible hydrogen content in deposited metal in different welding environments (air and water).

2. MATERIALS AND METHODS

The diffusible hydrogen content was measured in the deposited metal by general purpose OMNIA (E42 0 RC11) rutile electrodes that are 4.0 mm in diameter. The welding polarity was assumed to be in accordance with the electrode manufacturer recommendations (DC-), at a test stand 0.15 m deep under the water with the use Aristo 4000i as a welding power source. These electrodes were chosen because they provide good plastic properties of the weld metal, which minimizes the possibility of cold cracking in a water environment. The test stand is presented in Fig. 1. The weld beads were made on 4×20×120 mm specimens from S235JR steel. The chemical composition of the materials are presented in Table 1 and Table 2.

Determination of the diffusible hydrogen content with the glycerin method was carried out in accordance with standard procedure BN-64/4130-01 (1971). The test stand is presented in Fig. 2.

At first the specimen was weighed with an accuracy of 0.01 g before welding. The specimen was then placed in a copper fixture and the weld bead was deposited with a short arc. When the welding has been finished, the slag has been removed and the specimen was quenched in water at 20 °C. After 30 seconds, the specimen was cleaned, dried and placed in an apparatus. The time between finishing welding the sample and beginning the hydrogen content measurements did not exceed 2 min. The pressure, temperature and during extraction the temperature were measured. After being removed from the measurement vessel the specimen was cleaned, dried and weighed to determine the mass of deposited metal. Adjusting the results to normal operating conditions was completed according to the formula from BN-64/4130-01 (1971) standard. The glycerin solution was changed every two weeks as recommended (Fydrych and Łabanowski, 2015).

3. RESULTS

The tests were carried out on 10 specimens welded in the air (series 1 and 2) and 10 specimens made in the water environment (series 3 and 4). The first

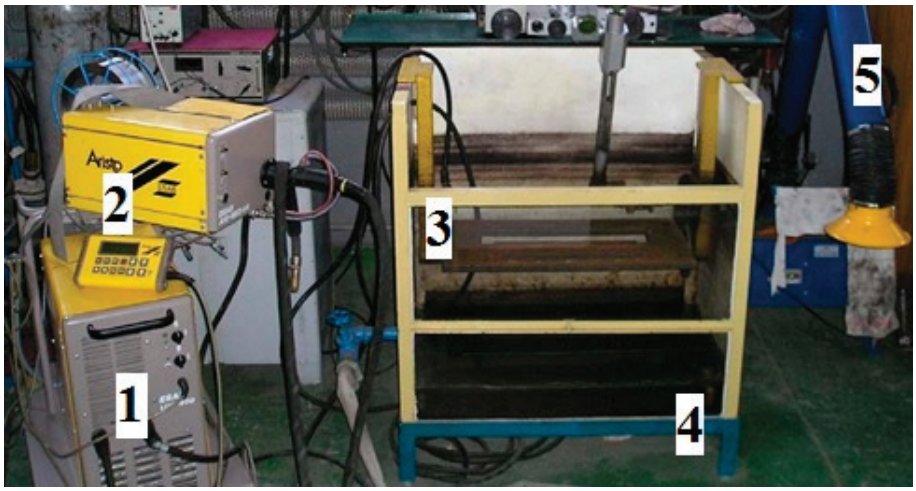

FIGURE 1. The experimental setup: 1) welding power source, 2) control panel, 3) table, 4) tank, and 5) welding extractor fan.

TABLE 1. Chemical composition of S235JR steel (wt,%)

C*	Mn*	P*	S*	N*	Cu*
0.17	1.4	0.035	0.045	0.012	0.55

*max

TABLE 2. Chemical composition of Omnia electrodes (wt,%)

C*	Mn*	P*	Si*	Cr*	Cu*
0.07	0.55	0.01	0.44	0.04	0.05

*max

part of the specimens was welded immediately after opening the package of the electrodes (series 1 and 3). Then the electrodes were stored in an open packages in laboratory conditions (temperature in range 18-21 °C, and humidity 50-60%), and they had direct contact with the air. After 3 years, the second part of the samples (series 2 and 4) was made to verify the effect of the storage time of electrodes on the diffusible hydrogen content in deposited metal in different welding environments. Additionally, the visual testing of electrode covering surfaces showed no changes in their appearance. The results of the determination of the diffusible hydrogen content are presented in Table 3. The exemplary specimens are presented in Fig. 3.

The results showed in Table 3 were subjected to statistical analysis. The first aim of the analysis was to verify is there was any statistically important difference in the diffusible hydrogen content for the specimens made in two environments. The second aim was to verify the effect of the storage time of electrodes on the diffusible hydrogen content in deposited metal in different welding environments.

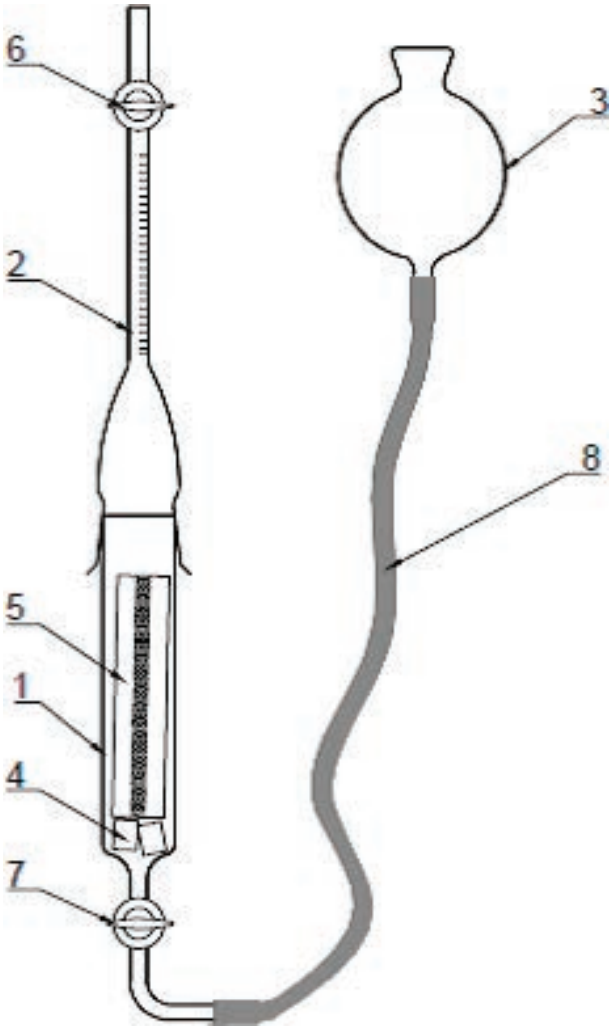

FIGURE 2. The schema of the glycerin measurement stand: 1) cylindrical vessel, 2) measurement vessel, 3) compensatory tank, 4) rubber washers, 5) sample, 6) upper valve, 7) lower valve, and 8) rubber hose.

TABLE 3. Results of the determination of the diffusible hydrogen content in deposited metal from the glycerin method

WELDED IN THE AIR							
Series 1				Series 2 (after 3 years)			
No.	ql (kJ·mm^{-1})	V (ml)	H_D (ml/100g)	No.	ql (kJ·mm^{-1})	V (ml)	HD (ml/100g)
1	0.85	2.8	34.20	**6**	0.88	3.0	32.61
2	0.83	3.3	32.65	**7**	0.85	3.3	33.43
3	0.88	2.9	34.28	**8**	0.91	3.1	39.95
4	0.91	3.1	33.70	**9**	0.87	2.9	36.03
5	0.92	2.9	36.59	**10**	0.90	3.8	37.73
WELDED IN THE WATER							
Series 3				Series 4 (after 3 years)			
11	0.62	2.1	51.50	**16**	0.73	3.1	59.93
12	0.63	4.1	59.69	**17**	0.70	3.3	57.85
13	0.63	3.0	58.80	**18**	0.63	3.2	61.34
14	0.63	3.9	56.42	**19**	0.62	1.6	58.20
15	0.62	2.0	55.09	**20**	0.62	2.9	59.12

FIGURE 3. Exemplary specimens after pad welding, first three – welded in the water, second three – welded in air

TABLE 4. Shapiro-Wilk test results

Series	Shapiro-Wilk statistic	p significance level
1	0.9130	0.4856
2	0.9542	0.7675
3	0.9508	0.7428
4	0.8754	0.2891

TABLE 5. Levene test results

MS effect	MS error	F	p
3.518778	1.864825	1.886921	0.172498

4. DISCUSSION

The statistical analyses were performed in a Statistica software package using the ANOVA module (one-way analysis of variance) with an assumed significance level $\alpha = 0.05$. In the first stage, a comparison of average results was carried out as a variable that groups a series of tests (type of environment and time of welding). Random variables in the considered populations (groups) are independent and measurable. It is necessary to verify the normal distribution of variables in each population and the homogeneity of variance in all populations. The assumption of normality was verified by the Shapiro-Wilk test. Based on the results shown in Table 4, it was assumed that the assumption is met ($p > \alpha = 0.05$).

The homogeneity of variance was verified by the Levene test. Because the *p* value is bigger than the assumed level of significance $\alpha = 0.05$, the assumption is met. The Levene test results are presented in Table 5.

The results of the variance analysis for all of the series are summarized in Table 6. Equality of means hypothesis test should be rejected because the value of $p < \alpha = 0.05$. It means that there is a statistically significant difference in the hydrogenation levels of the analyzed specimens.

In the next step, post-hoc analyzes were made. The aim was to determine which averages are significantly different. Scheffe, Tukey, NIR Fisher, Newman-Keuls and Duncan tests were used.

TABLE 6. Analysis of variance results

-	SS	Degree of freedom	MS	F	p
Intercept	4307.19	1	43072.19	7277.365	0.000000
Series	2575.74	3	858.58	145.063	0.000000
Error	94.70	16	5.92	-	-
4	0.8754	0.2891			

TABLE 7. Post-hoc test results

Series	Average diffusible hydrogen content [ml/100g]	Group 1	Group 2
1	34.284	****	
2	35.950	****	
3	56.300		****
4	59.094		****

Results obtained in different environments were assigned to two separate groups. It was shown that welding environment changes cause statistically significant differences in the level of the hydrogenation of the deposited metal. The post-hoc results are presented in Table 7.

Possible changes in the diffusible hydrogen content in deposited metal resulting from storage time of electrodes (3 years) were verified by Student's t-test. Table 8 presents the results of the analyzes for results obtained in the air environment and Table 9 presents results obtained in the water environment. In both environments, the values of $p > \alpha = 0.05$, so it was assumed that there are no significant differences in the content of hydrogen in a series of samples made before and after the three year period.

The graphical results of the analysis are presented in Fig. 4. Vertical error bars representing 0.95 confidence intervals overlap for series 1 and 2 (air environment) and 3 and 4 (water environment). There is a significant difference between results in different welding environments.

The literature stated, that the storage time of welding consumables could provide to increasing of the diffusible hydrogen content in deposited metal (Kiefer, 1996; Harwig *et al.*, 1999). The results of presented in this paper experiment proved the statement that storage time of the electrodes has resulted in the hydrogenation of electrodes covering, which was affected by moisture in the air. The expected result was an increase in the diffusible hydrogen content in deposited metal in the specimens made under water, which is due to the increase in the potential hydrogen amount in the welding environment (Tomków *et al.*, 2018c). The increase in the content of potential hydrogen caused by this phenomenon has no impact on the statistically significant increase

TABLE 8. Student's t-test results for series 1 and 2 (welding in the air environment)

Average diffusible hydrogen content series 1(ml/100g)	Average diffusible hydrogen content series 2(ml/100g)	T	df	p
34.284	35.950	-1.11046	8	0.299059

TABLE 9. Student's t-test results for series 3 and 4 (welding in the water environment)

Average diffusible hydrogen content series 3(ml/100g)	Average diffusible hydrogen content series 4(ml/100g)	T	df	p
56.300	59.094	-1.77273	8	0.114210

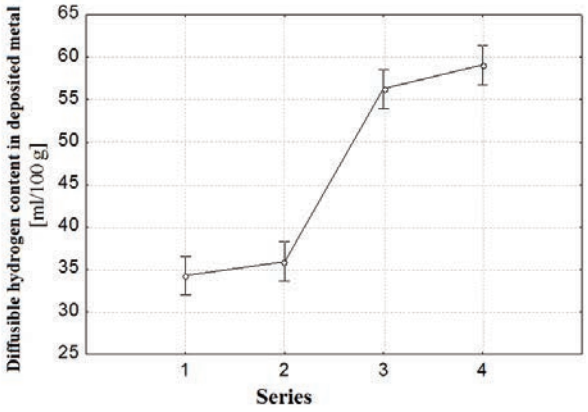

FIGURE 4. Diagram of the average values of diffusible hydrogen content in deposited metal. 1 - welding in the air, Series 1, 2 - welding in the air, Series 2, 3 - welding in the water, Series 3, 4 - welding in a water, Series 4.

in the diffusible hydrogen content in deposited metal. This was observed for welding experiments done in the air and in the water. The key achievement of presented results is statement that in the case of rutile electrodes, the storage time can be at least three years without changes in their appearance and harmful effect on hydrogenation of deposited metal. The key achievement of presented results is statement that in the case of rutile electrodes, the storage time can be at least three years without changes in their appearance and harmful effect on hydrogenation of deposited metal.

5. CONCLUSIONS

– Welding with rutile Omnia electrodes generates diffusible hydrogen content in the range from 32.61 to 39.95 ml/100 g in the air environment and in the range from 51.50 to 61.34 when welding in the water. It was shown that changes in the environment cause statistically significant changes in the diffusible hydrogen content.

– Three years of storing the electrodes in an opened package in laboratory conditions with contact with the air has no statistically significant influence on the diffusible hydrogen content in deposited metal regardless of the welding environment.

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