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DETERMINATION OF DIFFUSIBLE HYDROGEN CONTENT IN THE DEPOSITED METAL OF RUTILE ELECTRODES BY THE GLYCERIN METHOD

OZNACZANIE ILOŚCI WODORU DYFUNDUJĄCEGO W STOPIWIE ELEKTROD RUTYLOWYCH METODĄ GLICERYNOWĄ

Abstract

The presence of diffusible hydrogen in welded joints is one of the causes of formation the welding imperfections. Improvement of weldability can be achieved by reducing the hydrogen amount in welded joints. This requires, among others, the finding of sources of hydrogen. For high hydrogen processes the commonly used method of determining the diffusible hydrogen amount is the glycerin method. This paper concerns issues related to the test procedure and the possibility to control the diffusible hydrogen amount in deposited metal.

Key words: *diffusible hydrogen, rutile electrode, glycerin method*

Streszczenie

Obecność wodoru dyfundującego w złączach spawanych jest jedną z przyczyn powstawania niezgodności spawalniczych. Poprawę spawalności stali można osiągnąć przez zmniejszenie nawodorowania złączy. Wymaga to m.in. wyznaczenia źródeł wodoru. W procesach wysokowodorowych często stosowaną metodą oznaczania ilości wodoru dyfundującego jest metoda glicerynowa. Praca dotyczy zagadnień związanych z procedurą badawczą i możliwością sterowania ilością wodoru dyfundującego w stopiwie.

Słowa kluczowe: *wodór dyfundujący, elektrody rutylowe, metoda glicerynowa*

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1. Introduction

One of the main issues related to the metallurgy of welding processes is the effect of hydrogen on welded joints [1÷3]. High temperature accompanying welding promotes the penetration of hydrogen into the welding pool and then into other areas of the joints. The presence of hydrogen causes the formation of cold cracks, porosity and the embrittlement of steel [1÷4]. Moreover, issues associated with the measurements of the amount of hydrogen in welded joints are of interest for many years, as this quantity is one of the criteria for the classification of welding consumables [3÷9]. PN-EN ISO 3690:2012 [5] recommends, for the determination of the amount of diffusible hydrogen in the deposited metal, the usage of the mercury method, but very often also the glycerin method is used [3÷12]. Both methods are based on a collection of hydrogen extracted from the welded sample above the appropriate medium (glycerin, mercury), the measurement of its volume after 72 h of exposure, by relating to the weight of the deposited metal and the calculation of values relative to the normal conditions [5, 6, 9]. Figure 1 shows the test stands for the determination of the diffusible hydrogen amount in the deposited metal.
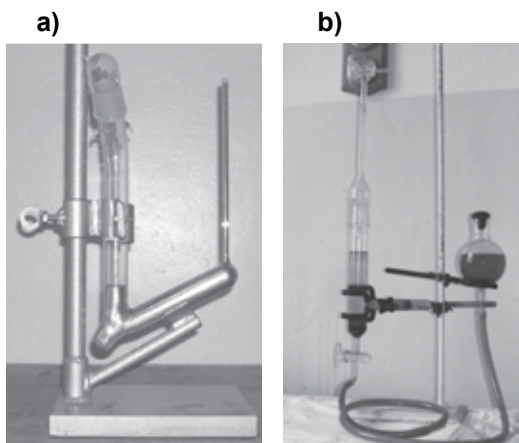
a)   **b)**

Fig. 1. Test stands for determining the amount of diffusible hydrogen in the weld metal: a) the mercury method, b) the glycerin method

The differences in the results obtained using different measuring methods are mainly the result of a different solubility of hydrogen in the liquids used in test [4, 7, 9, 11]. The effect of this phenomenon, which determines the accuracy of test methods can be compensated through the use of equations that describe the relationship between the results from the glycerin and the mercury methods [3, 4, 11]. Research carried out in the Laboratory of Welding Metallurgy of Gdańsk University of Technology allowed for the determination of such a relationship in the following form [11]:

$$H_{Dglyc} = 0.789 \times H_{Dmerc} - 2.13 \qquad\qquad (1)$$

where:

H_{Dglyc} – diffusible hydrogen amount in the deposited metal from the glycerin method [ml/100g Fe],

H_{Dmerc} – diffusible hydrogen amount in the deposited metal from the mercury method [ml/100g Fe].

Factors affecting the accuracy of the determination of the hydrogen content can be divided into procedural, which are associated with research methodology and technology concerning the preparation of deposited metals. The first group includes: the test fluid, the time and the temperature of the extraction of hydrogen, the time between the end of the surfacing of the sample and the beginning of determining, while the second group includes: the environmental conditions during surfacing, the chemical composition and the structure of the material, the parameters of test welding, the contamination of the adhesive and the sample, the conditions of storage and the drying of the filler materials, the application of the electrode used previously [4÷12].

The separate group of factors which have an effect mainly on the interpretation of the results are the conditions differentiating the methodology of making of the measurements of the phenomena occurring in the welding joints in the actual welded structures. These include the differences regarding: the dimensions of the sample, the number of beads, the initial temperature of the sample, and above all, relating the amount of diffusible hydrogen to the weight of the deposited metal instead of the weight of melted metal (weld) [3, 4, 8, 13÷14].

There is only limited information concerning the impact of not following an examination procedure and the conditions of coating of welding electrodes on the result of measuring the amount of diffusible hydrogen in the deposited metal. More frequently, studies have focused on the effect of welding parameters, the dimensions of samples, the environmental conditions, and also evaluating the relationship between the results of various measurement methods and their interlaboratory reproducibility [4, 10÷14].

2. Experimental

The aim of this study was to quantify the effect of the delay time for the beginning of the determination and the effect of the condition of welding electrode coatings on the amount of diffusible hydrogen in deposited metal. The study was conducted using the glycerin method.

The scope of the study included carrying out the following experiments:
– an evaluation of the impact of the delay time concerning the beginning the glycerin test on the diffusible hydrogen amount in the deposited metal by determining its amount in deposited metal from covered electrodes as delivered (start the extraction of hydrogen after 3, 9 and 15 min after the end of welding),
– an evaluation of the impact of the moisturizing time of the covered electrodes on the amount of diffusible hydrogen in deposited metal by determining its amount in the deposited metal of the electrodes as delivered and moisturized by immersion in water for 5, 30 and 720 min.

For the study samples of carbon structural steel S235JR and ER2.46 (E 382 RB 12 acc. to PN-EN ISO 2560:2010P) covered electrodes with a diameter of 4 mm were used. The chemical composition and mechanical properties of the base material and filler metal are summarized in Tables 1 to 3.

Determining the diffusible hydrogen amount in deposited metal was carried out using the glycerin method acc. to standard procedure [3, 6÷10]. To make test welds welding machine ESAB ARISTO 400 and power source ESAB LUC 400 were used.

Table 1. The chemical composition of S235JR steel

C_{max} [%]	Mn_{max} [%]	P_{max} [%]	S_{max} [%]	N_{max} [%]	Cu_{max} [%]
0.17	1.4	0.035	0.045	0.012	0.55

Table 2. The chemical composition of the deposited metal of electrodes ER 2.46 [15]

C [%]	Si [%]	Mn [%]
0.08	0.15	0.6

Table 3. The mechanical properties of the deposited metal of electrodes ER 2.46 [15]

Re [MPa]	R_m [MPa]	A_5 [%]
410	490÷560	24÷30

The first part of the study involves a determination of the amount of diffusible hydrogen in the deposited metal of the electrodes ER2.46 as delivered, wherein the 3, 9 and 15-minute time interval between the end of the surfacing and placing the sample in a measuring burette of test stand was maintained. Conditions, results of the experiments and mean values of three determinations are summarized in Table 4 and shown in Figure 2. As expected, the extension of the delay time caused a decrease in the amount of diffusible hydrogen in the deposited metal.

Table 4. Results of the study on the effect of extraction delay time on the diffusible hydrogen amount in the deposited metal

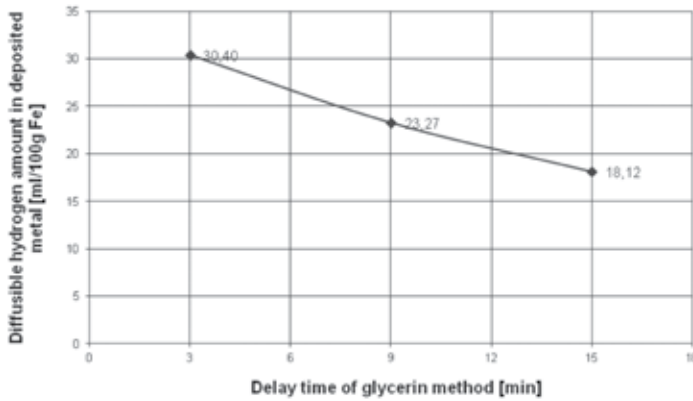| No.	The delay time of extraction of hydrogen [min]	The diffusible hydrogen amount in the deposited metal [ml/100g Fe]	The average diffusible hydrogen amount in the deposited metal [ml/100g Fe]	The diffusible hydrogen amount in the deposited metal [%]
1	3	29.81	30.40	100%
2		28.13		
3		33.28		
4	9	25.47	23.27	73.64%
5		22.82		
6		21.52		
7	15	20.08	18.12	57.3%
8		17.31		
9		16.97		

Fig. 2. Effect of delay time of the glycerin method on diffusible hydrogen amount in the deposited metal

On the basis of the results an equation of form (2) was designated.

$$H_{Dglyc} = -7,45 \times \ln t_o + 38.84 \qquad (2)$$

where:
H_{Dglyc} – the diffusible hydrogen amount in deposited metal [ml/100g Fe],
t_o – the delay time of the extraction of hydrogen [min].

The determination coefficient is $R^2 = 0.98$, indicating very good fit of the line to the experimental results [16].

The second part of the study consisted of determining the effect of time of wetting the covered electrodes ER2.46 on the diffusible hydrogen amount in the deposited metal. Moisturizing was carried out by immersing the electrodes in a container with water for 5, 30 and 720 min. Also the hydrogen content in the electrodes of the same species as delivered was determined. The time of beginning the extraction of hydrogen was 3 min. The results are shown in Table 5 and in Figure 3. As expected, longer time of moisturizing caused an increase of diffusible hydrogen content in deposited metal.

Table 5. Results of study on the effect of the moisturizing time of the electrodes on the diffusible hydrogen amount in deposited metal

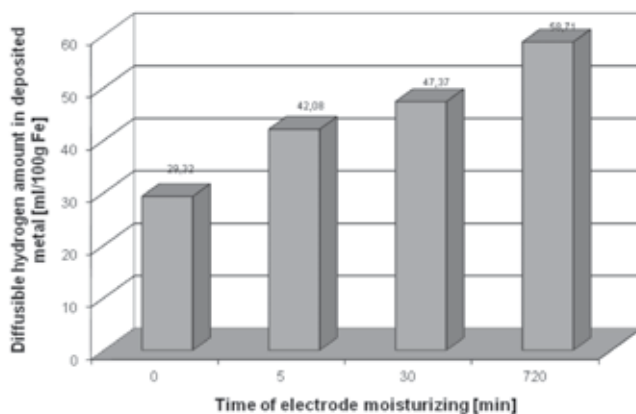| No.	The moisturizing time of electrodes [min]	The diffusible hydrogen amount in deposited metal [ml/100g Fe]
1	as delivered – 0 min	29.32
2	moisturized 5 min	42.08
3	moisturized 30 min	47.37
4	moisturized 720 min	58.71

Fig. 3. Effect of the moisturizing time of the electrode on the diffusible hydrogen amount in the deposited metal

The relationship between the wetting time of the rutile electrode and diffusible hydrogen content has the following form:

$$H_{Dglyc} = 3{,}29 \times \ln t_n + 36.73 \qquad\qquad (3)$$

where:
H_{Dglic} – the diffusible hydrogen amount in the deposited metal [ml/100g Fe],
t_n – the moisturizing time of the electrode [min].

The determination coefficient for the equation is $R^2 = 0.99$.

3. Discussion

This paper concerns issues related to the determination of the amount of diffusible hydrogen in deposited metal, relevant for the laboratory and industrial practice. The first one is associated with standard test procedure, the second refers to the possibility of determining the amount of diffusible hydrogen in the deposited metal on the demand level, which is particularly important during making the research of weldability.

The need for performing the studies resulted from the inconclusive state of the art regarding the considered issues and the necessity to control the accuracy of the measurement test stands located in the Laboratory of Welding Metallurgy of Gdańsk University of Technology.

The results obtained in the first stage of the study allow for a quantitative assessment of the measurement error introduced by a failure to comply of one of the basic conditions of the procedure of the glycerin method determining the diffusible hydrogen amount in the deposited metal (Fig. 4). Extension of the time from the end of the welding and cooling of the sample to placing it in the measuring burette from 3 to 9 min causes a decrease in the indications of the hydrogen content on average of about 23%, and with a delay of 15 min the error increases by an average of about 40%. This justifies the rigorous adherence to the recommendations for placing the sample in a test stand immediately after the completion of the welding.
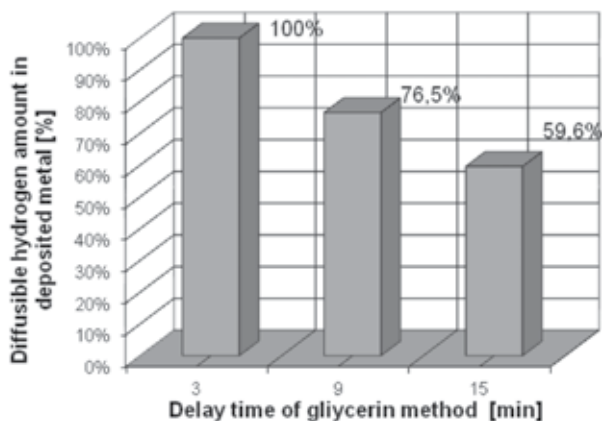
Fig. 4. Effect of delay time of the glycerin method on diffusible hydrogen content in the eposited metal

Experiments carried out in the next part of the study allow for the prediction of the amount of diffusible hydrogen in the deposited metal of covered electrodes subjected to moisturizing by the immersion in the water. As expected, prolongation of the wetting results in an increase of the diffusible hydrogen amount in the deposited metal, wherein the relationship is non-linear (logarithmic).

Both stages of the studies have been completed by the determination of the mathematical relationships describing the considered phenomena in the following forms:

$$H_{Dglyc} = -7{,}45 \times \ln t_o + 38.84$$
$$H_{Dglyc} = 3{,}29 \times \ln t_n + 36.73$$

where:
H_{Dglyc} – the diffusible hydrogen amount in the deposited metal [ml/100g Fe],
t_o – the delay time of the extraction of hydrogen [min],
t_n – the moisturizing time of the electrode [min].

Developed equations are characterized by high values of coefficients of determination. The results provide the basis for further research and analysis aimed at the determination of hydrogen sources during underwater welding with covered electrodes.

4. Conclusions

Based on the results it can be concluded that:
1. testing of susceptibility of the procedures of determination the diffusible hydrogen amount in deposited metal using glycerin method on the prolongation of the delay time at the beginning of the extraction was conducted and the determination of the effect of the moisturizing time of the rutile covered electrodes on the diffusible hydrogen amount in the deposited metal was carried out.

2. the equations for the evaluation of the measurement error of the glycerin method resulting from the failure of the procedural conditions and for predicting the diffusible hydrogen amount in the deposited metal moisturized covered electrodes were designated.
3. extension of time to placing the sample in the measuring burette from 3 to 9 min causes decrease of results by an average of 23%, and with a delay of 15 min, by 40%.
4. results of the studies can be used to evaluate the hydrogen sources during wet welding with the covered electrodes in the water environment.

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