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TECHNOLOGIES FOR PRODUCING LOW-HYDROGEN FUSED FLUXES

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ABSTRACT

The influence of the technology of producing welding fused fluxes on the content of hydrogen in them and nature of its thermal desorption was investigated. From the fluxes produced by the method of duplex process (sequentially operating gas-flame and electric-arc furnace), hydrogen is mainly removed at temperatures to 600 °C. It was established that the content of diffusion hydrogen in the deposited metal in welding under the fused fluxes, produced by the method of duplex process, is approximately by 30 % lower compared to fluxes produced in gas-flame furnaces. The use of fused semi-products in the composition of a charge while producing agglomerated fluxes was proposed.

KEYWORDS: hydrogen, automatic arc welding under the fused fluxes

INTRODUCTION

Hydrogen embrittlement and the formation of pores in welds are common, dangerous and insufficiently studied causes of fracture of many steel metal structures [1, 2]. In welding of high-strength steels under the influence of a thermal cycle in the metal, the formation of structures is probable, which, on the one hand, contribute to the significant strengthening of the metal, and on the other hand, increase its tendency to the formation of cold cracks [3, 4]. The ability of metal to resist the initiation and propagation of cold cracks is improved when the concentration of diffusion hydrogen in it decreases. The conditions were established, under which the risk of formation of cold cracks in welded joints is reduced to a minimum. Thus, in the case of limiting the cooling rate of the metal in the temperature range of 600-500 °C to 10 °C/s, and the content of diffusion hydrogen in the deposited metal to 4 $cm^3/100$ g, the stress level that can be withstood by the metal of the heat-affected zone (HAZ) of welded joints of steels with a carbon equivalent $C_e = 0.35 - 0.45$ % without the formation of cold cracks, amounts to 90 % of its yield strength [5].

It is generally known that the main cause for the formation of pores in the welds during welding steels is an increased content of hydrogen in the welding pool metal and its release at the moment of crystallization as a result of an abrupt decrease in solubility [6]. The hydrogen content in the weld metal, in excess of which pores are formed in the welds during welding of low-alloy steels under manganese-silicate fluxes, amounts to 12–14 cm³ per 100 g of weld metal [7].

The arc in automatic submerged arc welding burns in a closed envelope created by a molten slag and a layer of flux. The access of hydrogen to the arc zone Copyright © The Author(s) from the outside is complicated. The sources of saturation of the welding pool with hydrogen are flux, oil and rust on the surface of the welding wire and on the metal edges to be welded. Moreover, the flux is determined as the main source of hydrogen. Therefore, it is important to study the content of hydrogen in welding fused fluxes and the process of its thermal desorption, the creation of technologies for the production of low-hydrogen welding fused fluxes.

PROCEDURE FOR STUDIES OF HYDROGEN CONTENT IN WELDING FLUXES

In order to control the processes of fluxes dehydration in the process of their production and use in welding, it is important to know the peculiarities of the course of the process of its desorption during the heating process. To measure the content of potential hydrogen in the coatings of electrodes, fluxes, cores of flux-cored wires, a method [6] of gradual heating of specimens to a temperature of about 1000 °C in an argon flow with conversion of compounds containing hydrogen was proposed. To avoid errors in the measurement of hydrogen due to the release of O₂, N₂, CH₄, CO and CO₂, a chromatographic method of analysis was proposed, which has high sensitivity and separation ability for the abovementioned compounds. As a result of the constant heating rate, it is possible both to determine the total water content at a temperature of 900-1000 °C, as well as to determine the nature of its bond with the substance under study (hygroscopic, adsorbed on the surface of grains, crystal hydrate, crystallization, zeolitic, dissolved in the form of OH groups). The error in measuring the amount of hydrogen is not more than 7 %. Each peak of thermal desorption in the chromatograms is a peak of hydrogen evolution. The hydrogen content was recalculated on 100 g of the substance under study using a graduated factor of 0.57 mm³ H_2 /mBC obtained immediately before this work was carried out.

STUDY OF THE INFLUENCE OF FLUX MELTING TECHNOLOGY ON THEIR HYDROGEN CONTENT

In general, the technology of producing welding fused fluxes involves melting charge materials in a flux melting furnace, producing a homogeneous melt of the required chemical composition with the following granulation. Granulation provides obtaining flux grains of the required size and bulk weight. After granulation, fluxes are calcined, dispersed in appropriate sieves and delivered to the user. Depending on the chemical composition and technical requirements for fluxes, different types of furnaces (gas-flame and electric-arc) and methods of granulation (wet, into water) and dry (in air) can be used [8]. Until recently, Ukraine ranked first in the world in terms of production of fused fluxes. In Ukraine, fluxes of the MnO-SiO₂-CaF₂ slag system are produced most massively (more than 80 % of the total volume). These are general-purpose glass-type fluxes (AN-348A, OSTs-45, AN-348V and ANTs-1) for welding carbon and low-alloy steels and pumice-like fluxes (AN-60, AN348AP, OSTs-45P) for high-speed welding of steel structures of the same type. The first are usually produced in gas-flame furnaces, and the latter in electric-arc furnaces. In both cases, fluxes are granulated into water. Namely, the fluxes of this slag system were taken as objects for research. The aim of the work was to study the influence of technological factors on the hydrogen content at various stages of producing welding fused fluxes. The work was performed in industrial equipment at the facilities of PRJSC "Zaporizhskloflus". This equipment is composed of gas-flame and electric-arc flux melting furnaces installed side by side with the possibility of their simultaneous operation. This makes it possible to direct the slag melt from one furnace to another (duplex process). Granulation can also be performed both in wet (into water) as well as in dry (into metal moulds) method.

Gas-flame and electric-arc flux melting furnaces differ in temperatures, to which the slag melt is brought. In the gas-flame furnace, the temperature does not exceed 1400 °C, and in the electric-arc furnace it can reach 1700 °C. Therefore, in order to determine the influence of the temperature of the slag melt on its hydrogen content, AN-348AP flux was produced by the method of duplex process. In the course of melting, samples were taken first at the outlet from the gas-flame furnace, then at the outlet from the electric-arc furnace. The temperature of the slag melt during sampling was determined by an optical pyrometer. These samples were calcined on a thickwalled metal surface, as a result of which a glass-type structure was obtained and preserved until the analvsis in a sealed container, which made it impossible for them to absorb moisture from the surrounding atmosphere. The research results given in Table 1, showed that the hydrogen content in the slag melt in the gas-flame furnace at the melt temperature of 1400 °C was 40.6 cm³/100 g (sample 1), in the electric-arc furnace at the melt temperature of 1530 °C it was 14.8 cm³/100 g (sample 2).

When the temperature was further increased to 1700 °C, the hydrogen content in AN-348AP flux melt decreased to 6.9 cm³/100 g (sample 3). It should be noted that not only the temperature of the slag melt determined the final hydrogen content in it. The decrease in hydrogen content is also explained by better conditions for removing hydrogen from the melt in the electric-arc furnace compared to the gas-flame furnace due to more intensive mixing of the melt. In addition, during the combustion of gas in the atmosphere of the gas-flame furnace, a significant amount of water vapours accumulates (up to 15 % by analogy with steel-making furnaces). Therefore, even a significant exposure of the melt in this furnace and the use of low-hydrogen raw materials will not allow reducing the content of dissolved hydrogen in the melt below a certain limit. On the contrary, in the electric-arc furnace, there are conditions for an additional reduction in the concentration of hydrogen in the molten slag, because the probability of removing gases released from the melt during melting through gas extractors exists. In addition, intensive burning of the carbon lining and graphite electrodes leads to a decrease in the concentration of hydrogen in the slag, as is the case in steel melting slags.

Thus, the technology of flux melting using the method of duplex process leads to a decrease in the

Table 1. Hydrogen content in fluxes at different stages of production

Flux	Type of flux melting furnace	Temperature of slag melt in the furnace, °C	Hydrogen content in the slag melt, cm ³ /100 g	Hydrogen content in the finished flux after wet granulation, cm ³ /100 g	
AN-348A	Gas-flame	1400	40.6 (sample 1)	44 (sample 4)	
AN-348AP	Duplex-process	1700	6.9 (sample 3)	62 (sample 5)	



Figure 1. Chromatograms of thermal desorption of hydrogen from fluxes: a - AN-348A flux (sample 4) H = 44 cm³/100 g (gas-flame furnace); b - AN-348AP flux (sample 5) H = 62 cm³/100 g (duplex process)

hydrogen content in the slag melt by approximately 6 times compared to flux melting in the gas-flame furnace. It is clear that during dry granulation, the hydrogen content in the finished flux remains at the level of its content in the slag melt. The influence of melt granulation into water on the total hydrogen content in the flux remains unexplored. In order to find out this issue, the melts were granulated during sampling 1 and 3 according to the usual technology for the production of fluxes in the gas-flame and electric-arc furnaces. After granulation, the fluxes were calcined in the industrial drum dryers that provided a temperature of the flux at the output from the drying drum of 250-300 °C, as is determined by the technological documentation for the production of fluxes, were dispersed and packed. At this stage, the hydrogen content of the specimens taken from the bags as-delivered was investigated.

It was established that the temperature of the melt before the start of granulation significantly affects the final hydrogen content in the flux. Thus, at a slag melt temperature of 1400 °C, the grains with a glass-type structure are formed. At the same time, the hydrogen content after wet granulation increases by approximately 10 % (from 40.6 to 44 cm³/100 g (final hydrogen content in AN-348A flux (sample 4)). When a slag melt heated to a temperature of 1700 °C comes into contact with water, a vapour envelope with high water vapour pressure forms around the melt particles. Considering the low viscosity of the slag melt at such temperatures, cavities are formed in the flux particles, occupying up to 80 % of the total volume of the flux. These cavities are filled with water vapours, which condenses during cooling. In general, this leads to an increase in the hydrogen content in the flux by

approximately 9 times (from 6.9 to 62 cm³/100 g (final hydrogen content in AN-348AP flux (sample 5)).

The studies of thermal desorption of hydrogen showed that the main part of moisture from AN-348AP flux is removed while heating to 600 °C (in contrast to AN-348A flux, from which hydrogen is removed at temperatures close to the melting point of the flux and, of course, enters the welding pool). To confirm this fact, Figure 1 shows chromatograms of thermal desorption of hydrogen from AN-348A flux — gas-flame furnace + granulator — sample 4) and AN-348AP flux – duplex process + granulator sample 5).

To reduce the hydrogen content in the fused flux, the use of electric-arc furnace or the duplex process while melting flux can be recommended, which allow bringing the melt to a temperature of 1700 °C and using dry granulation fluxes. However, for the fluxes of the studied MnO-SiO₂-CaF₂ slag system, the use of the duplex process is more appropriate. In addition to limiting the hydrogen content, the duplex process provides a significant reduction in the content of sulphur and phosphorus in fluxes and, at the same time, prevents undesired increased losses of the main components in fluxes of this slag system. As a result, the dependence on scarce, expensive high-quality raw materials is reduced and the possibility of using wastes of metallurgical, welding and mining production in the production of fluxes is achieved, and their competitiveness grows [9, 10]. In order to reduce the hydrogen content in the flux produced by the method of duplex process, it was proposed to bring the melt to a temperature of 1700 °C, hold it at this temperature, then lower the temperature of the melt to 1400 °C and only then granulate it into water. To check these



Figure 2. Chromatograms of thermal hydrogen desorption: a — OSTs-45 flux (gas-flame furnace) $H = 36 \text{ cm}^3/100\text{g}$; b — OSTs-45M flux (duplex process) $H = 30 \text{ cm}^3/100 \text{ g}$

recommendations, the content and nature of thermal desorption of hydrogen from vitreous flux OSTs-45 (gas-flame furnace) and glass-type flux OSTs-45M (duplex process) were investigated. OSTs-45M flux was produced by heating the melt to 1700 °C, holding the melt at this temperature for 20 min, cooling the melt to 1400 °C and granulating it into water. Comparing the fluxes produced by the method of duplex process (OSTs-45M and AN-348AP), it should be noted that the total hydrogen content in OSTs-45M flux is 2 times lower than that of AN-348AP flux (30.0 and 62 cm³/100 g respectively). This can be explained by the fact that the melt of OSTs-45M flux is cooled to a temperature of 1400 °C before granulation. As a result, a flux with a glass-type grain structure is formed. Comparing OSTs-45 and OSTs-45M fluxes, which differ in the production method, it is worth noting that both fluxes have the similar glass-type grain structure. The total hydrogen content in OSTs-45M flux $(30 \text{ cm}^3/100 \text{ g})$ compared to OSTs-45 flux produced in the gas-flame furnace $(36 \text{ cm}^3/100 \text{ g})$ is slightly lower. It was found that these fluxes differ significantly in the nature of hydrogen desorption during heating process (Figure 2). From Table 2 and the chromatograms of fluxes produced in the gas-flame furnace (AN-348A,

OSTs-45), it is seen, that the main amount of hydrogen is removed at temperatures close to the melting point of the flux (990 °C). The fluxes produced by the method of duplex process (OSTs-45M and AN-348AP) are characterized by the fact that hydrogen desorption from them occurs at lower temperatures (mainly up to 800 °C). Even for pumice-like AN-348AP flux, which has a high total hydrogen content (62 cm³/100 g), only 9.3 cm³/100 g is released during exposure at 990 °C. For glass-type OSTs-45M flux, this value amounts to 8.7 cm³/100 g of flux.

At the next stage of studies, the influence of the total content of hydrogen in the fluxes and the nature of its thermal desorption on the content of diffusion hydrogen in the deposited metal during welding was determined. The content of diffusion hydrogen in the metal of welds was determined by the method of chromatographic analysis according to GOST 23338–91 using OB 2178 gas analyzer designed at PWI. The objectivity of the results of measuring the amount of diffusion hydrogen is predetermined by the fact that the hydrogen released from the specimen in a sealed metal chamber is measured by the method of gas chromatography. The reliability of the results of measuring the content of diffusion hydrogen is con-

Table 2. Total content and nature of thermal desorption of hydrogen in welding fluxes

Flux	Production method		Grain	Total content	Amount of hydrogen removed during heating in the temperature range, cm ³ /100 g/%				
	Type of furnace	Granulation method	structure	(<i>H</i>), cm ³ /100 g	0–20 °C	200–600 °C	600–800 °C	990 °C	Higher than 990 °C
AN-348A	Cas flama		Vitreous	44	2.6/6	4.0/9	5.3/12	3.5/8	28.6/65
OSTs-45	Gas-name	- Wet		36	1.8/5	4.0/11	5.0/14	9.7/27	15.5/43
OSTs-45M	Duplex			30	4.5/15	6.9/23	5.4/18	4.5/15	8.7/29
AN-348AP	process		Pumice-like	62	24.2/39	14.2/23	6.9/11	7.4/12	9.3/15

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Place and la	Content of hydrogen in flux,	Content of hydrogen in metal, cm ³ /100 g		
Flux grade	cm ³ /100 g of flux	[H] _{diff} , deposited metal	[H] _{res} , weld	
AN-348A	44	6.8; 7.4; 7.7/ 7.3	2.2; 2.4; 2.6/ 2.4	
AN-348AP	62	4.7; 5.2; 5.4/ 5.1	1.6; 1.6; 1.7/ 1.6	

Table 3. C	ontent of hyd	rogen in	fluxes and	deposited	metal
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firmed by numerous comparative tests of it with the mercury method of analysis according to ISO 3690 standard [11].

The specimens to analyse the content of diffusion hydrogen in the deposited metal were produced by the method of depositing a bead on an assembled specimen of 10G2FB steel. Before welding, the specimens were kept at a temperature of 800 °C for 1 h. The welding wire of Sv-10G1NMA grade with a diameter of 4 mm was stripped from the coppered coating and degreased. The surfacing was carried out on a direct current of reverse polarity on the mode: $I_{\rm m}$ = = 550–600 A, U_a = 32–34 V, V_w = 36 m/h. The parameters of the welding mode were determined from the conditions of providing the input energy required by GOST 23338–91 (not more than 3 kJ/mm), producing welds with geometric dimensions that allow an easy separation of the specimen from the run-off tabs (with width up to 22 mm and height up to 6 mm). The deposited specimen was cooled with water at a temperature of 0 °C for 3 s and immersed in liquid nitrogen. When a temperature of 196 °C was reached, the run-off tabs were removed, and the specimen was preserved in liquid nitrogen before carrying out the analysis. Three specimens were produced for each flux sample. Immediately before welding, all fluxes were calcined at a temperature of 300 °C for 1 h. The content of diffusion hydrogen was calculated according to ISO 3690.

From Table 3, it is seen that the content of diffusion hydrogen in the deposited metal when using the technology of duplex process in the production of flux is approximately by 30 % lower compared to the traditional technology of melting fluxes in the gas-flame furnace. At the same time, from the results of studying the nature of thermal desorption of hydrogen, shown in Figure 1 and in Tables 2, 3, it is seen that the content of diffusion hydrogen in the deposited metal is determined not by the total content of hydrogen in the flux, but by the amount of hydrogen removed from the flux at temperatures close to their melting point. It is clear that this hydrogen cannot be removed from fluxes by calcination of fluxes at a temperature of 300-400 °C for 1 h recommended by GOST 9087-81, which should be performed immediately before welding. It is known from [12], that such hydrogen is dissolved in the form of OH groups during melting in the furnace.

I.e., the amount of dissolved hydrogen is determined by the method of flux production.

Taking into account the obtained positive results regarding the reduction of hydrogen content in welding fused fluxes produced by the technology of duplex process, the use of fused semi-products in the charge of agglomerated welding fluxes is promising.

CONCLUSIONS

1. It was established that the technology of melting flux using the method of duplex process leads to a decrease in the total hydrogen content in the slag melt by almost 6 times compared to melting flux in the gasflame furnace.

2. When pouring the slag melt into water during granulation, the hydrogen content in the flux increases nonuniformly depending on the initial temperature of the melt: by 10 % at a melt temperature of 1400 °C and approximately 9 times at a melt temperature of 1700 °C.

3. It was established that depending on the temperature of the slag melt before granulation into water, the nature of thermal desorption of hydrogen changes. The main amount of hydrogen from the glass-type fluxes granulated at a melt temperature of 1400 °C is removed at temperatures close to their melting point (over 990 °C). For pumice-like fluxes, granulated at a melt temperature of 1700 °C, the main part of hydrogen is removed at temperatures of up to 800 °C.

4. Recommendations for the creation of technology for the production of low-hydrogen fused fluxes were developed. To reduce the hydrogen content in the fused flux, it was recommended to use the duplex process when melting the flux, which allows bringing the melt to a temperature of 1700 °C and using dry granulation fluxes. In the case of wet granulation, it is necessary to bring the melt to a temperature of 1700 °C, maintain it at this temperature, then lower the temperature of the melt to 1400 °C and only then granulate it into water.

5. It was established that the content of diffusion hydrogen in the deposited metal when using welding fused fluxes produced by the method of duplex process is approximately 30% lower compared to the option of using fluxes produced in the gas-flame furnace.

6. In order to further reduce the hydrogen content in the weld metal, a promising direction is conducting research on the use of fused semi-products as part of the charge in the production of agglomerated fluxes.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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