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IMPROVEMENT OF THE TECHNOLOGY OF MANUFACTURING LOW-HYDROGEN AGGLOMERATED FLUXES USING FUSED MATERIALS

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ABSTRACT

Gas chromatography method was used to study thermal desorption of hydrogen from mineral raw materials, used in manufacture of agglomerated welding fluxes. The good prospects for application of fused materials in the charge composition in agglomerated flux manufacture were established. Increase of fused material content in the composition of agglomerated flux charge leads to lowering of the flux susceptibility to sorption of environmental moisture. At increase of the content of fused material in the agglomerated flux charge from 15 up to 40 % the diffusible hydrogen content in the deposited metal decreases from 3.5 to 2.6 cm^3/100 g in submerged-arc welding with these fluxes.

KEYWORDS: hydrogen, automatic arc welding with agglomerated fluxes, low-alloy steels

INTRODUCTION

Metal structures from high-strength low-alloy (HSLA) steels have been ever wider introduced into production over the recent years [1, 2]. In high-strength steel welding the metal under the influence of the thermal cycle can form structures which, on the one hand promote considerable strengthening of the metal, and on the other hand, increase its cold cracking susceptibility [3, 4]. Metal ability to resist cold crack initiation and propagation becomes higher with lowering of diffusible hydrogen concentration in it. Conditions were determined, under which the risk of cold cracking in welded joints is minimized. So, in the case of limiting the metal cooling rate to 10 °C/s in the temperature range of 600–500 °C and diffusible hydrogen content to 4 cm^3/100 g in the deposited metal, the level of stresses, which the metal of the HAZ of welded joints on steels with carbon equivalent C_e = 0.35–45 % can withstand without cold cracking, is equal to 90 % of its yield limit [5].

Considering the analysis of changes in the requirements to strength and ductility of high-strength low-alloy steels, a vast majority of the authors come to the conclusion that these requirements cannot be met when welding with the currently available fused fluxes [6, 7]. Thus, there is no alternative to the choice of agglomerated fluxes in high-strength steel welding. Their wide introduction in Ukraine is held back by absence of modern industrial production. In works [8, 9] the authors, while noting the advantages of agglomerated fluxes, also mention their inherent disadvantages, which are determined by their manufacturing method: higher susceptibility to environmental moisture sorption, lower strength of flux granules and dependence of flux quality on the quality of raw materials used in its manufacture. As regards the latter shortcoming, it needs an additional explanation. Owing to absence of pyrometallurgical and high-temperature processes in the liquid slag in agglomerated flux manufacture, it is impossible to lower the content of such impurities as sulphur, phosphorus, structural moisture and organic compounds in the charge material composition. Considering the higher level of requirements to the content of impurities in welding HSLA steels, the quality of agglomerated fluxes is largely determined by the quality of raw materials used in their manufacture. The high-quality raw materials necessary for agglomerated flux manufacture is either absent or very expensive in Ukraine. This is exactly the cause for absence of industrial production of agglomerated fluxes in Ukraine – the country where the first agglomerated fluxes were developed. On the other hand, at manufacture of fused fluxes there are capabilities for melt refining to remove impurities, and a high-capacity industrial production of fused fluxes is available, Ukraine taking the first place by the volumes of their manufacture until recently. It creates opportunities for development of a new technology of agglomerated flux manufacture, based on application of fused materials. In work [10] a conclusion is made about using fused materials, made by duplex-process technology, in the charge in manufacture of low-hydrogen agglomerated fluxes. Such materials have a low total content of sulphur, phosphorus and hydrogen. Thermal desorption of hydrogen from them occurs at up to 800 °C temperatures.

The objective of this work was determination of the influence of adding fused materials to the charge composition on their susceptibility to sorption of environmental moisture, and diffusible hydrogen content in the deposited metal in welding with the developed agglomerated fluxes.

PROCEDURES FOR STUDYING HYDROGEN CONTENT IN RAW MATERIALS AND DIFFUSIBLE HYDROGEN IN THE DEPOSITED METAL

Total content of hydrogen in raw materials was determined by the chromatographic method, having a high sensitivity to hydrogen, and resolution with respect to O_2, N_2, CH_4, CO, CO_2, H_2O [11]. It allows determination of both the total hydrogen content in the studied materials, and the process of hydrogen desorption at their heating up to the temperature of 1100 °C.

Diffusible hydrogen content in weld metal was determined by chromatographic analysis to GOST 23338°91 with application of OB 2781P gas analyzer. Sample heating temperature was 150 °C, which allowed reducing the hydrogen measuring time. The objectivity of the results of measuring the volume of diffusible hydrogen is due to the fact that hydrogen, which evolved from the sample in a sealed metal chamber, is measured by gas chromatography method. The reliability of the results of measuring the diffusible hydrogen content is confirmed by numerous comparative tests with mercury analysis method to ISO Standard 3690:2018 [12].

Samples for analysis of diffusible hydrogen content in the deposited metal were produced by bead deposition on a composite sample from 10G2FB steel with application of welding wire of Sv-10G1NMA grade at DCRP in the following mode: I_w = 550–600 A, U_a = 32–34 V, V_w = 36 m/h. Sample preparation and determination of diffusible hydrogen content in the deposited metal was performed to ISO 3690:2018.

INVESTIGATION OF HYDROGEN CONTENT IN RAW MATERIALS FOR AGGLOMERATED FLUX MANUFACTURE

Technology of agglomerated flux manufacture, unlike that of fused flux manufacture, has limited capabilities for lowering their hydrogen content. Raw materials are the main source of hydrogen in manufacture of agglomerated welding fluxes. That is why it is important to use non-traditional raw materials with limited hydrogen content. Conducted analysis of wastes of Ukrainian industrial enterprises showed that from such materials the most suitable for flux manufacture is granulated slag from silica manganese production and slag crust, which forms in welding large-diameter pipes. Table 1 gives their compositions.

These materials are remelted products and contain only a small amount of hydrogen, namely slag crust — 25 cm^3/100 g; and granulated slag from silica manganese production — 198 cm^3/100 g. Hydrogen is present in them in the form of moisture absorbed on their surface, which is readily removed by baking at up to 300 °C temperature.

Analysis of hydrogen content was performed in raw materials which can be used in manufacture of agglomerated fluxes for welding. Investigations showed that hydrogen content is more than 1500 cm^3/100 g in G-OO alumina, and 6300 cm^3/100 g is periclase. Considering the high content of hydrogen in these materials, its content was also studied in other materials, which contain magnesium and aluminium oxides. In particular, conducted investigations showed that hydrogen content in white corundum of 25 A grade is equal to 92 cm^3/100 g, and in periclase powder for PPE-88 electric furnaces it is 1156 cm^3/100 g. Such a hydrogen level in materials is critical in terms of their applicability for agglomerated flux manufacture. That is why the influence of raw material heat treatment on their hydrogen content was studied. Thermogravimetric and differential thermal analyses of the above-mentioned materials were also performed in the range from 20 to 1000 °C. Such a study was conducted in air, and its purpose was to determine whether undesirable oxidation of the raw materials will occur simultaneously with hydrogen desorption from them at their baking. It was found that for the raw materials given below heat treatment at 900 °C is optimal, allowing hydrogen content in quartz sand to be lowered from 240 to 15 cm^3/100 g, in white corundum of 25A grade — from 92 to 10 cm^3/100 g, in fluorite concentrate — from 340 to 10 to 15 cm^3/100 g, in periclase powder for PPE-88 electric furnaces — from 1156 to 10 to 15 cm^3/100 g, and in fused flux — from 60 to 10 to 15 cm^3/100 g. It is proposed to conduct baking of charge materials for agglomerated flux manufacture at the temperature of 900 °C for 1 h before granulation.

It is understandable that high-temperature baking of raw material components in agglomerated flux manufacture is rather energy efficient. Investigations of the remelted products — slag crust and slag from silica manganese production showed that they have low total content of hydrogen and lower (up to 300 °C) temperature of removal of hydrogen-containing compounds. Therefore, it is promising to apply fused materials, including those made by duplex-process technology in agglomerated flux charge, to limit their hydrogen content.

Table 1. Chemical composition of granulated slag from silica manganese production and slag crust of AN-60 welding flux

Material name	Chemical composition, wt.%									
	SiO_2	MnO	CaF_2	CaO	Al_2O_3	MgO	FeO	P_2O_5	SO_2	Rest
Slag from silica manganese production	48.0	20.0	–	14.0	8.0	5.0	0.3	0.008	1.0	3.7
Slag crust of AN-60 flux	40.0	35.0	7.0	8.0	4.0	2.0	4.0	–	–	–

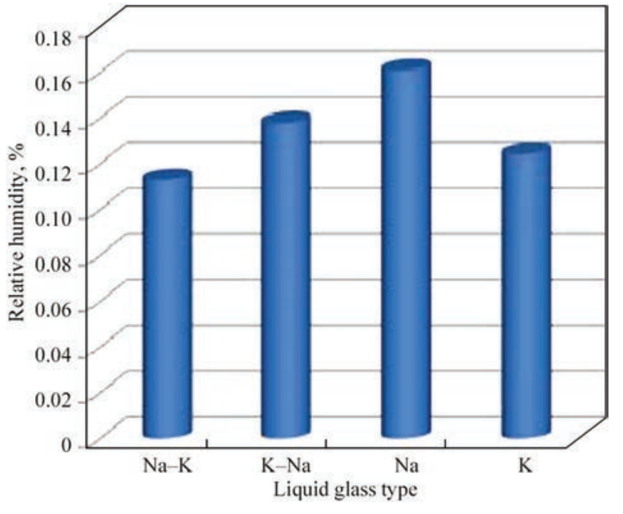

Figure 1. Influence of liquid glass type in the agglomerated flux charge on their susceptibility to moisture absorption

INVESTIGATIONS OF THE SUSCEPTIBILITY TO AMBIENT AIR MOISTURE SORPTION BY AGGLOMERATED FLUXES, HAVING FUSED MATERIALS IN THE CHARGE COMPOSITION

Technology of agglomerated flux manufacture is based on irreversibility of the process of dehydration of the liquid glass component during flux heat treatment. The final product of liquid glass dehydration is a strong, dense and moisture-resistant silicate film, having a certain resistance to environmental moisture absorption. The liquid glass type essentially influences the agglomerated flux susceptibility to moisture sorption (Figure 1).

Evaluation of the kinetics of sorption-induced moisture absorption by the fluxes was performed during which flux samples, baked at the temperature of 400 °C for 2 h before the experiment were soaked in the desicator with constant humidity of 77.6 % and temperature of 22 ± 0.5 °C. The lowest sorption capacity was demonstrated by agglomerated fluxes based on Na–K liquid glass.

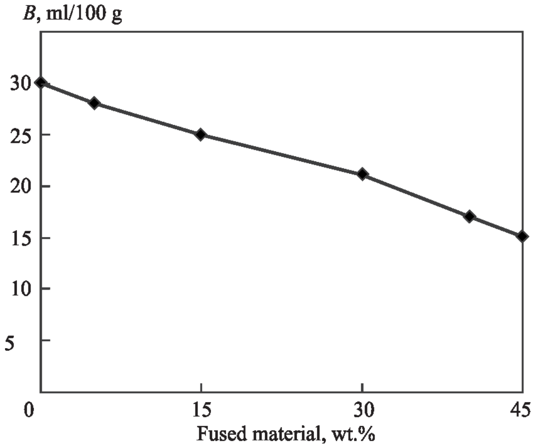

Figure 2. Dependence of liquid glass consumption at granulation of agglomerated flux on fused material content

Experimental agglomerated fluxes of MgO–Al_2O_3–SiO_2–CaF_2–TiO_2–ZrO_2 system were manufactured, which differed by the content of fused material in their composition. Screenings of AN-47 flux to GOST 9087 made by duplex-process, were taken as the fused material.

It was found that increase of the content of fused materials up to 45 %, in the agglomerated flux charge composition, which, in our opinion, have smaller specific surface compared to the traditional raw materials, leads to reduction of the quantity of binder required for granule formation from 30 to 15 % (Figure 2).

Content of liquid glass dry residue largely determines the agglomerated flux susceptibility to moisture absorption. This is confirmed by the results of comparative studies of fused and agglomerated fluxes based on mineral raw materials with different content of fused materials (Figure 3).

Increase of fused material content to 45 % leads to lowering of the flux sorption capacity by 46 %, and by this characteristic such flux is close to fused flux with glassy grain structure and it is superior to agglomerated aluminate basic fluxes, made by the traditional technology. In our study agglomerated OP-132 flux of Oerlikon Company, and fused manganese-silicate fluxes with pumice-like (AN-60) and glassy (AN-348A) grain structure were used for comparison.

INVESTIGATIONS OF DIFFUSIBLE HYDROGEN CONTENT IN THE DEPOSITED METAL IN WELDING WITH AGGLOMERATED FLUXES

Diffusible hydrogen content in the deposited metal was studied in welding with agglomerated fluxes of MgO–Al_2O_3–SiO_2–CaF_2–TiO_2–ZrO_2 system, which differed

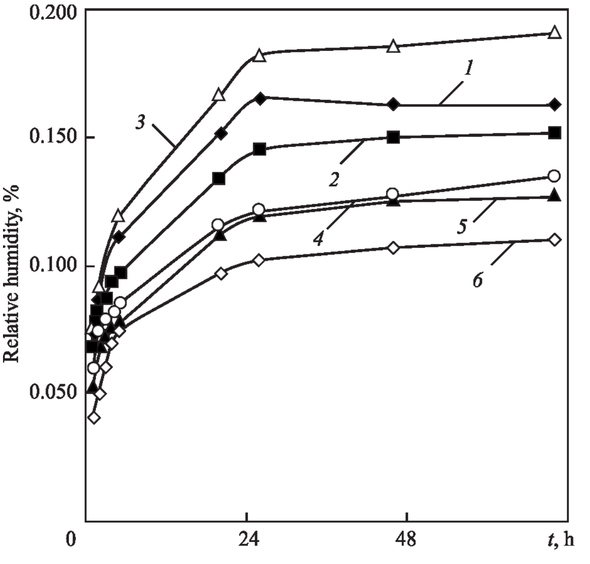

Figure 3. Influence of fused material content and technology of welding flux manufacture on flux susceptibility to sorption of environmental moisture: *1* — 15 % of fused material; *2* — 30 % of fused material; *3* — basic agglomerated aluminate; *4* — fused pumicelike manganese silicate; *5* — 45 % of fused material; *6* — fused glassy manganese silicate

Table 2. Influence of fused material content in agglomerated flux composition on diffusible hydrogen content in the deposited metal

Number	Content of fused material in the agglomerated flux charge composition	Diffusible hydrogen content $[H]_{dif.\ dep.\ metal}$, $cm^3/100$ g
1	15	3.2; 3.9; 3.5
2	40	2.6; 2.7; 2.3

by the content of fused material in their composition. Screenings of AN-47 flux to GOST 9087 made by duplex-process were taken as the fused material.

Investigation results are given in Table 2.

One can see from Table 2 that increase of fused material content from 15 to 40 % in the charge composition leads to reduction of the content of $[H]_{dif.\ dep.\ metal}$ below 3 $cm^3/100$ g. In keeping with the classification proposed by IIW, at $[H]_{dif.\ dep.\ metal}$ level below 5 $cm^3/100$ g welding electrodes are regarded as such which ensure a very low diffusible hydrogen content in the deposited metal [11]. Modern agglomerated fluxes of the leading world manufacturers provide $[H]_{dif.\ dep.\ metal}$ of up to 5 $cm^3/100$ g. Therefore, it can be considered that agglomerated fluxes, having fused materials manufactured by duplex-process in their charge composition, ensure extremely low hydrogen content in the deposited metal.

CONCLUSIONS

1. Gas chromatography method was used to study the total hydrogen content in mineral raw materials, applied in manufacture of agglomerated welding fluxes. It is proposed to conduct baking of charge materials for manufacture of agglomerated fluxes at the temperature of 900 °C for 1 h before granulation. The good prospects for application in the charge composition of wastes of Ukrainian industrial enterprises, which are remelted products and which contain a small quantity of hydrogen was established, namely slag crust of fused welding flux AN-60 (25 $cm^3/100$ g) and granulated slag of silica manganese production (198 $cm^3/100$ g). It was established that hydrogen is present in these materials in the form of moisture absorbed on the surface, which is readily removed by baking at up to 300 °C temperature.

2. It is found that increase of the content of fused materials in the charge composition of agglomerated fluxes up to 45 % leads to reduction of the quantity of binder required for flux granules formation from 30 to 15 %.

3. Increase of the content of fused material in the composition of agglomerated flux charge to 45 % leads to lowering of sorption capacity of the fluxes by 46 % and by this characteristic such fluxes are close to fused fluxes with glassy grain structure and are superior to agglomerated aluminate basic fluxes, made by the traditional technology.

4. With increase of the content of fused material in the composition of the agglomerated flux charge from 15 to 40 % the diffusible hydrogen content in the deposited metal in welding with agglomerated fluxes drops from 3.5 to 2.6 $cm^3/100$ g.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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