New welding fluxes based on silicomanganese slag for deposition and welding of canopies and crib bed of mine support

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Abstract. The paper considers the possibility of efficient use of silicomanganese slag for the production of welding fluxes. The results of studying the use of metallurgical wastes as components of welding fluxes are given. Analysis of the results of mechanical properties of the samples made it possible to determine the optimum content of the pulverized fraction less than 0.45 mm in the flux. The composition and technology of manufacturing a new welding flux using slag of silicomanganese production was developed. The effect of fractional composition on the welding-technological properties of fluxes was studied. The optimal content of liquid glass in the flux, which allows a favorable complex of mechanical properties to be obtained, is 20-30%. To reduce the level of contamination of the weld metal with non-metallic oxide inclusions and to increase the mechanical properties of the welded joint, it is proposed to introduce a carbon-fluorine-containing additive FD-UFS into fluxes based on the slag.

1. Introduction
Today much attention is paid to creation, research and development of new welding fluxes both in the Russian Federation and abroad [1 - 18]. The use of silicomanganese slag for the manufacture of welding fluxes is proposed [19, 20], the technology is protected by patents [21, 22].

2. Methods of research
The chemical composition of the examined surfaced samples was determined according to GOST 10543-98 (Russian National Standard) by the X-ray fluorescence method on XRF-1800 spectrometer and by the atomic-emission method using DFS-71 spectrometer. The metallographic analysis was carried out using OLYMPUS GX-51 optical microscope in a bright field in the magnification range ×100-1000 after etching in alcoholic nitric acid solution. The grain size was determined in accordance with GOST 5639-82 at magnification ×100. Investigation of longitudinal samples of the surfaced layer for the presence of nonmetallic inclusions was made in accordance with GOST 1778-70 at magnification of × 100.

3. Results and discussion
For flux preparation slag of silicomanganese production was used (its chemical composition is given in table 1), while in the first series of experiments the possibility of using a different ratio of slag fractions was investigated (table 2). Butt-welding under fluxes was performed without a double bevel on the samples with dimensions 500×75 mm, thickness 16 mm, from sheet steel grade 09G2S. The
process was carried out using S-08GA wire and ASA-1250 welding tractor in the following modes: \( I = 700 \, \text{A}; \, U = 30 \, \text{V}; \, V = 35 \, \text{m/h}. \)

From the welded plates the samples were cut and X-ray spectral analysis of the composition of weld metal and metallographic examinations of weld metal were performed. The chemical composition of welding fluxes is given in Table 3. The chemical composition of the slag crust is given in Table 4, the chemical composition of weld metal is given in Table 5.

| Sample | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 |
|--------|----|----|----|----|----|----|----|----|----|----|----|
| Al_2O_3 | 6.91 | 9.62 | 9.62 | 9.62 | 9.62 | 9.62 | 9.62 | 9.62 | 9.62 | 9.62 | 9.62 |
| CaO    | 22.85 | 31.70 | 31.70 | 31.70 | 31.70 | 31.70 | 31.70 | 31.70 | 31.70 | 31.70 | 31.70 |
| SiO_2  | 46.46 | 48.16 | 48.16 | 48.16 | 48.16 | 48.16 | 48.16 | 48.16 | 48.16 | 48.16 | 48.16 |
| FeO    | 0.27 | 0.81 | 0.81 | 0.81 | 0.81 | 0.81 | 0.81 | 0.81 | 0.81 | 0.81 | 0.81 |
| MgO    | 6.48 | 7.92 | 7.92 | 7.92 | 7.92 | 7.92 | 7.92 | 7.92 | 7.92 | 7.92 | 7.92 |
| MnO    | 8.01 | 8.43 | 8.43 | 8.43 | 8.43 | 8.43 | 8.43 | 8.43 | 8.43 | 8.43 | 8.43 |
| F      | 0.28 | 0.76 | 0.76 | 0.76 | 0.76 | 0.76 | 0.76 | 0.76 | 0.76 | 0.76 | 0.76 |
| Na_2O  | 0.26 | 0.36 | 0.36 | 0.36 | 0.36 | 0.36 | 0.36 | 0.36 | 0.36 | 0.36 | 0.36 |
| K_2O   | below | 0.62 | 0.62 | 0.62 | 0.62 | 0.62 | 0.62 | 0.62 | 0.62 | 0.62 | 0.62 |
| S      | 0.15 | 0.17 | 0.17 | 0.17 | 0.17 | 0.17 | 0.17 | 0.17 | 0.17 | 0.17 | 0.17 |
| P      | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |

Table 1. Chemical composition of slag of silicomanganese production.

Table 2. Fractional and component compositions of the investigated fluxes.

Table 3. Chemical composition of welding fluxes.

Table 4. Chemical composition of slag crusts.

The results of the analysis for the presence of nonmetallic inclusions in the weld zone, carried out in accordance with GOST 1778-70, are shown in Figure 1 and in Table 5.
Figure 1. Nonmetallic inclusions in the weld zone of samples: 

a – 1; b – 2; c – 3; d – 4; e – 5; f – 6; g – 7

Table 5. Chemical composition of weld seams metal.

| Sample | C  | Si  | Mn  | Cr  | Ni  | Cu  | V   | Nb  | Al  | S   | P   |
|--------|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1      | 0.09 | 0.71 | 0.51 | 0.03 | 0.10 | 0.11 | 0.001 | 0.014 | 0.023 | 0.018 | 0.012 |
| 2      | 0.08 | 0.54 | 1.33 | 0.04 | 0.05 | 0.08 | 0.003 | 0.014 | 0.015 | 0.008 | 0.008 |
| 3      | 0.09 | 0.61 | 1.49 | 0.04 | 0.11 | 0.11 | 0.01 | 0.013 | 0.018 | 0.016 | 0.010 |
| 4      | 0.07 | 0.45 | 1.24 | 0.02 | 0.05 | 0.07 | 0.002 | 0.014 | 0.014 | 0.006 | 0.007 |
| 5      | 0.08 | 0.66 | 1.42 | 0.03 | 0.10 | 0.11 | 0.002 | 0.015 | 0.023 | 0.018 | 0.012 |
| 6      | 0.08 | 0.61 | 1.42 | 0.02 | 0.06 | 0.08 | 0.003 | 0.014 | 0.029 | 0.010 | 0.011 |
| 7      | 0.08 | 0.59 | 1.39 | 0.02 | 0.02 | 0.05 | 0.004 | 0.018 | 0.091 | 0.014 | 0.009 |
| 8      | 0.05 | 0.52 | 1.25 | 0.02 | 0.04 | 0.05 | 0.003 | 0.017 | 0.020 | 0.005 | 0.007 |
| 9      | 0.03 | 0.51 | 1.23 | 0.02 | 0.04 | 0.06 | 0.002 | 0.017 | 0.017 | 0.007 | 0.008 |
| 10     | 0.06 | 0.55 | 1.31 | 0.02 | 0.04 | 0.06 | 0.004 | 0.016 | 0.018 | 0.012 | 0.009 |
| 11     | 0.09 | 0.52 | 1.31 | 0.02 | 0.04 | 0.06 | 0.003 | 0.015 | 0.013 | 0.010 | 0.008 |

The microstructures of weld seams metal are shown in figure 2.

Samples were cut from the welded plates and mechanical properties were determined. After studying their mechanical properties the results were obtained indicating an increase in the values of impact hardness (figure 3).

Figure 2. Microstructures of welded joints in the samples: a – 1; b – 2; c – 3; d – 4; e – 5; f – 6; g – 7
Figure 3. Influence of dust fraction content in the flux on the impact hardness.

Analysis of the mechanical properties of samples cut from the welded plates made it possible to establish that the optimum content of dust fraction less than 0.45 mm in the flux is 20-30%. With such content of dust fraction less than 0.45 mm in the flux, a favorable complex of mechanical properties of the samples cut from the welded plates is achieved.

In the structure of the weld metal of all samples ferrite is present in the form of non-equiaxed grains stretched in the direction of heat removal. The transition from a uniform ferrite-pearlite structure to the perlite and ferrite structure of vidmanstetten orientation can be seen. At the same time, the samples did not show a significant change in grain size on the grain scale (tables 6 and 7).

In the second series, the possibility of using a ceramic flux made of silicomanganese slag dust with a fraction up to 0.45 mm bound by liquid glass was studied. The manufacturing process consisted of mixing silicomanganese slag with liquid glass in various ratios (table 2), drying, crushing, sieving and obtaining a fraction of 0.45-2.5 mm.

Analysis of the results of mechanical properties of samples cut from welded plates made it possible to determine the optimal content of liquid glass in the flux (up to 20-30%) in order to achieve a favorable complex of mechanical properties of samples cut from welded plates (figure 4, 5).

However, the investigated fluxes are oxidizing and are based on the principles of silica-manganese-oxidation-reduction processes, in connection with which the products of these reactions are oxide compounds of silicon and manganese, thereby increasing the level of contamination of the weld metal with nonmetallic inclusions and, as a consequence, mechanical properties deteriorate, especially at low negative temperatures. To reduce the contamination of weld metal and improve mechanical properties, we considered the possibility of introducing the developed FD-UFS additive into a new flux.

| Sample | Non-deforming silicates | Non-deforming silicates | Non-deforming silicates |
|--------|------------------------|------------------------|------------------------|
| 1      | 4b; 3b; 4a             | 3b                     | 1a                     |
| 2      | 2b; 1b; 3a; 4a         | -                      | 1a; 2a                 |
| 3      | 4b; 2b                 | -                      | 1a; 2a                 |
| 4      | 2b; 4b                 | -                      | 1a; 2a                 |
| 5      | 4b; 5b; 3b             | -                      | 1a; 2a                 |
| 6      | 2b; 1b; 2a; 2.5a       | -                      | 1a; 2a                 |
| 7      | 2b; 2a; 2.5a           | -                      | 1a; 2a                 |
| 8      | 2b; 1b; 2a; 2.5a       | -                      | 1a                     |
| 9      | 2b; 1b; 2a; 2.5a       | -                      | 1a                     |
| 10     | 2b; 1b; 2a; 2.5a       | -                      | 1a; 2a                 |
| 11     | 2b; 2.5a               | -                      | 1a; 2a                 |
Table 7. The value of weld seam grains in accordance with GOST 5639-82.

| Sample | Grain size according to grain scale |
|--------|------------------------------------|
| 1      | No. 4, No. 5                       |
| 2      | No. 5, No. 4                       |
| 3      | No. 4, No. 5, No. 6                |
| 4      | No. 4                              |
| 5      | No. 5, No. 4                       |
| 6      | No. 4                              |
| 7      | No. 4                              |
| 8      | No. 5, No. 4                       |
| 9      | No. 4, No. 5                       |
| 10     | No. 4                              |
| 11     | No. 4, No. 5                       |

Figure 4. Influence of the content of liquid glass in the flux on the relative elongation.

In the experiments a flux additive to the new flux was used mixed in a ratio of 2, 4, 6, 8 %, respectively.
The chemical composition of the investigated crusts is given in table 8, the slag crust is given in table 9, the chemical composition of weld metal is given in table 10.

Thus, the highest level of contamination with nonmetallic inclusions is observed in the weld metal, made with a flux without an additive. The addition of FD-UFS additive reduces the level of contamination with non-metallic inclusions, reducing their size and quantity. In the investigated intervals the use of an additive in the amount of 8 % is more effective for reducing the level of contamination with nonmetallic inclusions.

**Table 8. Chemical composition of the investigated flux mixtures, %.**

| Content of FD-UFS in the flux, % | FeO | MnO | Ca | SiO₂ | Al₂O₃ | MgO | Na₂O | K₂O | S | P | ZnO | F |
|---------------------------------|-----|-----|----|------|-------|-----|------|-----|---|---|-----|---|
| 2                               | 0.40| 8.01| 15.80| 50.08 | 11.55 | 7.39 | 0.77 | 0.63 | 0.22 | 0.008 | 0.002 | 1.30 |
| 4                               | 0.91| 7.90| 17.72| 46.63 | 10.32 | 6.63 | 1.10 | 0.68 | 0.24 | 0.01 | - | 1.95 |
| 6                               | 0.81| 7.68| 16.79| 43.64 | 11.27 | 5.71 | 2.25 | 0.65 | 0.34 | 0.01 | 0.003 | 4.04 |
| 8                               | 0.46| 7.46| 16.00| 43.64 | 11.86 | 5.56 | 2.30 | 0.60 | 0.33 | 0.01 | 0.002 | 3.96 |

**Table 9. Chemical composition of slag crusts, %.**

| Content of FD-UFS in the flux, % | FeO | MnO | Ca | SiO₂ | Al₂O₃ | MgO | Na₂O | K₂O | S | P | ZnO | F |
|---------------------------------|-----|-----|----|------|-------|-----|------|-----|---|---|-----|---|
| 2                               | 2.21| 7.25| 15.55| 38.09 | 9.39 | 8.63 | 0.49 | 0.57 | 0.12 | 0.006 | 0.002 | 0.94 |
| 4                               | 2.28| 7.39| 16.90| 42.00 | 9.76 | 5.77 | 0.76 | 0.62 | 0.15 | 0.008 | 0.002 | 1.12 |
| 6                               | 2.24| 7.20| 16.06| 39.94 | 11.15 | 7.14 | 1.09 | 0.60 | 0.17 | 0.008 | 0.002 | 1.53 |
| 8                               | 2.36| 7.14| 14.70| 42.87 | 12.40 | 5.57 | 1.34 | 0.57 | 0.20 | 0.008 | 0.002 | 1.88 |

**Table 10. Chemical composition of weld seams.**

| Content of FD-UFS in the flux, % | C     | Si   | Mn   | Cr   | Ni   | Cu   | Nb   | Al   | S    | P    |
|---------------------------------|-------|------|------|------|------|------|------|------|------|------|
| 2                               | 0.09  | 0.62 | 1.40 | 0.02 | 0.06 | 0.09 | 0.014| 0.023| 0.020| 0.008|
| 4                               | 0.10  | 0.60 | 1.34 | 0.02 | 0.07 | 0.08 | 0.010| 0.013| 0.023| 0.009|
| 6                               | 0.12  | 0.66 | 1.43 | 0.02 | 0.06 | 0.10 | 0.011| 0.012| 0.027| 0.008|
| 8                               | 0.13  | 0.65 | 1.36 | 0.03 | 0.06 | 0.09 | 0.013| 0.013| 0.024| 0.008|

The results of the analysis for the presence of nonmetallic inclusions in the weld zone, carried out in accordance with GOST 1778 - 70, are shown in figure 6 and in table 11.

The microstructure of the weld seam of samples is shown in figure 7. It is established that the introduction of an additive in the amount up to 8 % does not affect the size and morphology of the structural components.

**Figure 6.** Nonmetallic inclusions in the weld zone of samples with additive %: a – 2; b – 4; c – 6; d – 8.
Table 11. Nonmetallic inclusions in the weld zone.

| Content of FD-UFS in the flux, % | Nonmetallic inclusions, point |
|---------------------------------|--------------------------------|
|                                 | non-deforming silicates | brittle silicates | spote silicates |
| 2                               | 2b, 4b, 5b               | -                  | 1a, 2a           |
| 4                               | 2b, 4b                   | -                  | 1a, 2a           |
| 6                               | 2b, 4b, 1b               | -                  | 1a, 2a           |
| 8                               | 2b                        | -                  | 1a, 2a           |

Figure 7. Microstructure of the weld seams of samples with an additive, %: a – 2; b – 4; c – 6; d – 8.

The study of the values of mechanical properties showed that they improve with the increase in the amount of FD-UFS additive (figure 8). The conducted researches formed the basis of patents of the Russian Federation [21, 22].

Figure 8. Influence of the content of FD-UFS additive in flux on the impact hardness (KCV at -20 °C).

4. Conclusions
1. The principal possibility of using slag of silicomanganese production for manufacturing welding fluxes is shown.
2. It is possible to use up to 30 % of fine fraction (less than 0.45 mm) in fluxes. With such a content of the dust fraction in the flux a favorable complex of mechanical properties of the samples cut from the welded plates is achieved.
3. Optimal content of liquid glass in the flux, which allows a favorable complex of mechanical properties to be obtained, is (20-30 %). This flux is recommended for deposition and welding elements of mechanized support.
4. It is proposed to introduce a carbon-fluorine-containing additive FD-UFS in the amount of 2-8 % to reduce the level of contamination of the weld metal with nonmetallic oxide inclusions and increase
the mechanical properties of the weld seam. The addition of FD-UFS additive reduces the level of contamination with nonmetallic inclusions, reducing their size and quantity.

References
[1] Puchol R Q et al 2009 Welding Int. 23(2) 132–40
[2] Crespo A C et al 2007 Welding Int. 21(7) 502–11
[3] Crespo A C et al 2009 Welding Int. 23(2) 120–31
[4] Golovko V V and Potapov N N 2011 Welding Int. 25(11) 889–93
[5] Volobuev Yu S et al 2012 Welding Int. 26(8) 649–53
[6] Potapov N N and Kurlanov S A 1987 Welding Int. 1(10) 951–4
[7] Babushkin P L and Persits V Yu 1991 Welding Int. 5(9) 741–2
[8] Pavlov I V and Oleinichenko K A 1987 Welding Int. 1(10) 951–4
[9] Chigarev V V and Kosenko A A 1994 Welding Int. 8(10) 808–9
[10] Kurlanov S A et al 1993 Welding Int. 7(1) 65–8
[11] Bablik O V and Chamov S V 2010 Welding Int. 24(9) 730–3
[12] Gur’ev S V et al 2012 Welding Int. 26(8) 646–8
[13] Parshin S G 2012 Welding Int. 26(10) 800–4
[14] Cruz-Crespo A et al 2005 Welding Int. 19(7) 544–51
[15] Bublik O V and Chamov S V 2010 Welding Int. 24(9) 730–3
[16] Barmin L N et al 1989 Welding Int. 3(2) 109–11
[17] Kazakov Yu V et al 1991 Welding Int. 5(3) 202–5
[18] Potapov N N et al 2009 Welding International 23(10) 800–3
[19] Kozyrev N A, Kryukov R E et al 2016 IOP Conf. Series: Materials Sci. and Eng. 125 012034
[20] Kozyrev N A, Kryukov R E et al 2016 IOP Conf. Series: Materials Sci. and Eng. 150 012032
[21] Kryukov N E, Kryukov E N, Kozyrev N A, Kryukov R E and Kozyreva O A 2016 Flux for Welding Patent of the Russian Federation 2576717, MPK8 V23 K35/362 publ. 03.10.2016 Bul. No. 7
[22] Kryukov N E, Kryukov E N, Kozyrev N A, Kryukov R E and Kozyreva O 2016 Flux for Welding Patent of the Russian Federation 2579412, MPK8 V23 K35/362 publ. 04.10.2016 Bul. No. 10