(Methods of usage of mathematical model for adjusting of continuous section rolling mills. *Proizvodstvo prokata* = Rolling production. 1999. № 5. P. 7–12.
11. Moller A.B. Adaptiruemaya matrichnaya model dlya povysheniya tochnosti nepreryvnoy sortovoy prokatki (Adaptive matrix model for increase of precision of continuous section rolling). The thesis for degree of candidate of technical sciences. Nosov Magnitogorsk state technical university. Magnitogorsk. 1996
12. Fedorov Yu. N.. Poryadok sozdaniya, modernizacii i soprovozhdeniya ASU TP (Order of creation, modernization and accompanying of automatic control system for technological processes). Moscow. *Infra-Inzheneriya* = Infra-Engineering. 2011. 576 p.

***V. E. Roshchin*[1], *N. V. Malkov*[1], *A. V. Roshchin*[1]**
[1] *South Ural State University, (Chelyabinsk, Russia)*
E-mail: Roshchinve@susu.ac.ru

Usage of worked-out metallurgical slag In electroslag remelting processes

There are economically and technically effective technologies of steel producing with low level of sulfur, phosphorous, oxygen and hydrogen in metal. As a consequence, there is no special need of refining metal from impurities in electroslag remelting. Remelting primary objective is to obtain a favorable structure while maintaining of low hydrogen content and increasing the technical and economic evidence of the remelting process itself. The new generation flux of low base-to-acid ratio based on worked-out metallurgical slag was developed. The physical, physico-chemical, technological properties of this flux, structure and properties of the investigated weld metal have been studied in laboratory and industrial conditions. The technical parameters of the process of ESR have been evaluated. It was shown that proposed flux is workable and its application provides consistently ESR process with a high speed, reduces electricity consumption up to 1,5 times and provides welding of metals with a good surface quality. Proposed flux protects the weld metal better from hydrogen saturation than widely used $CaF_2 - Al_2O_3$ flux ANF-6. The mechanical properties of cast metal, welded under this flux are close to forged steel after remelting under $CaF_2 - Al_2O_3$ flux.

Key words: *flux, slag recycling, electroslag remelting, metal refining, metal welding, hydrogen saturation, mechanical properties, sulfur, phosphorus, oxygen, hydrogen.*

1. Introduction

It's well-known that metallurgical enterprises, in addition to metal production, produce a lot of various slags (blast furnace slag, steelmaking slag, secondary metallurgy slags etc.). Pyrometallurgical companies engaged for a long time the challenge of the slag usage and solve it rather successfully. Nowadays, such slag is used for manufacture of building materials, roadway backfills, in the cement industry, in agriculture for liming the soil etc. [1], because it brings significant economic benefits (lower consumption of lime, alumina and the other additives, saving coke, recovering heat etc). Thus in Europe about 87% of worked-out pyrometallurgical slags nowadays are used at present time in building industry [2]. It must be noted, that blast furnace slag is the most suitable for recycling — it's recycled up to 100%, steelmaking slags are used less — about 79%, and the least used slag is slag of ferroalloy production industry. However, it's possible that the further requirements would be more environmentally concerned, taking into account targets like preservation and protection of the environment and humans. From that positions, using of metallurgical slags, especially from ferroalloys (because of self-disintegrate property, possibility of heavy / toxic compounds like Cr^{6+} forming and so on) in building could be restricted or even forbidden, so another usage of such materials should be find.

The chemical and granulometric composition and low price of ferroalloy slags make them challenging to reuse in the metallurgical industry, particularly as a starting materials for the production of low base-to-acid ratio and low-fluorine fluxes for electroslag remelting process (ESR).

ESR is used in the steel industry mainly for deep desulfurizaing, refining of metal from non-metallic inclusions and obtaining a dense cast structure of metal. To achieve these goals, a series of fluxes has been developed, which is based on the systems of calcium fluoride with thermodynamically strong oxides (calcium, aluminum and magnesium). These fluxes are characterized by high refining capability and they have a set of physical and physico-chemical properties. It allows to provide stable melting conditions. Wide circulation of flux from 70% mass. CaF_2 and 30% mass. Al_2O_3 (named ANF-6) was obtained in Russia.

Table 1. Chemical composition of initial materials							
Material	Chemical composition (mass %)						
	SiO_2	CaO	MgO	Al_2O_3	CaF_2	Cr_2O_3	Fe_Σ
Slag from high-carbon ferrochrome	30–35	4–6	30–35	20–30	–	10–15	≤5
Slag from silicocalcium silicothermic production	30–35	63–68	0–1	5–10	2–10	–	–
Magnesite powder	≤1	0–5	96–98	n/a	–	–	n/a
Quartz sand	95–99	n/a	n/a	0–4	–	–	n/a
n/a – not analyzed							

However, the scarce mineral CaF_2 is needed for such fluxes production, and in the process of refining from slag melt into the atmosphere evolves a big amount of fluorine compounds, negatively affecting on human health and wildlife. Beside that, fluoride melts have a high hydrogen permeability, it leads to increasing of [H] in remelted metal, lowering positive influence of ESR.

Nowadays there are economically and technically effective technologies of steel producing with low level of sulfur, phosphorous, oxygen and hydrogen in metal. As a consequence, there is no special need of refining metal from impurities in electroslag remelting. Remelting primary objective is to obtain a favorable structure while maintaining of low hydrogen content and increasing the technical and economical evidence of the remelting process itself. To solve this problem, the fluxes of low base-to-acid ratio should be used. In addition, the shortage of fluorspar (calcium fluoride), environmental unsafety of fluorine-containing fluxes lead to developing of fluxes with the lowest content of calcium fluoride.

The low base-to-acid ratio flux of the new generation for the ESR based on worked-out metallurgical slag have been developed at the Pyrometallurgical department of South Ural State University. It is based on the slag system $CaO–MgO–SiO_2–Al_2O_3$. The initial flux of the proposed composition is made as a mixture of lime, quartzite, alumina, calcined magnesite, and fluorspar [3–4]. The physical, physico-chemical, technological properties of this flux, structure and properties of the investigated weld metal have been studied in laboratory and industrial conditions. The technical parameters of the process of ESR have been evaluated.

The following materials are characterized by the next negative or unvalue points:

– Lime. Due to high requirements only fresh lime, produced from limestone in rotary or shaft furnace, should be used. The high cost of lime defined not only by the cost of calcinating, but also by the costs associated with the creation of special conditions of transportation and storage.

– Alumina. Costs are relatively high due to the complex scheme of alumina production, including production of agglomerate from bauxite, melting of agglomerate in the furnace to produce fused alumina, and then crushing of product for manufacture of alumina powder.

– Magnesium oxide is a product of the firing of magnesite in rotary kilns. The high cost of magnesite powder is also defined by the complex and energy intensive scheme of obtaining, special conditions of transportation and storage.

Based on the above-mentioned, the aim of the current research is the lowering the costs of ESR by reducing of flux costs by the usage of non-deficient or, preferable, waste materials as well as improving the technical and economic indices of the process of melting itself.

2. Experimental part

2.1. Sample preparation

The object of the study was low base-to-acid ratio low-fluorine fluxes, comprising (mass. %): 27–34 CaO, 34–40 SiO_2, 18–27 MgO, 5–10 Al_2O_3, 1–5 CaF_2. To obtain the flux of such composition, unused at the present time and non-deficient materials (crushed slag from high-carbon ferrochrome production and self-slaking slag from silicocalcium silicothermic production as well as quartz sand and magnesite powder) were used. The chemical composition of these materials is given in **Table 1**.

Materials were dosed in the desired ratio, mixed and interfused in a molybdenum crucible for laboratory research, and in flux melting furnace with a graphite crucible for industrial research.

2.2. Measurements

The melting temperature of experimental flux, the influence of temperature on the electrical conductivity, viscosity and evaporation rate (volatility) and the technological properties of the slag were determined in the laboratory conditions.

The melting point was determined by differential thermal analysis (DTA), the electrical conductivity by the voltmeter — amperemeter scheme from Ohm's law, viscosity — by vibration method, and the evaporation rate — by the gravimetric method (by flux mass loosing).

The technological properties of experimental flux in the laboratory were examined at the laboratory ESR unit to obtain the ESR ingot weighing about 3 kg. Electrodes of diameter 35 mm made from 40Cr steel were melted in the 50 mm diameter mold. The surface quality of ingot, melting rate, the consumption of electrical energy, the thickness of scull were controlled.

Industrial experiments were carried out at ESR facilities for obtaining ingots weighing about 2.5 tons. Remelting was carried out in the mobile and the stationary molds, a process began either with solid (or "cold") or liquid ("hot") starting. The speed of melting, the consumption of electrical energy, the thickness of scull, surface quality of the ingot were controlled. Samples of metal for determination of hydrogen content in liquid metal were taken in the course of melting.

Weld metal quality was controlled in the cast and deformed state. In the cast metal, chemical composition during the ESR, macrostructure of the upper, middle and bottom parts of the ingot, content of nonmetal-

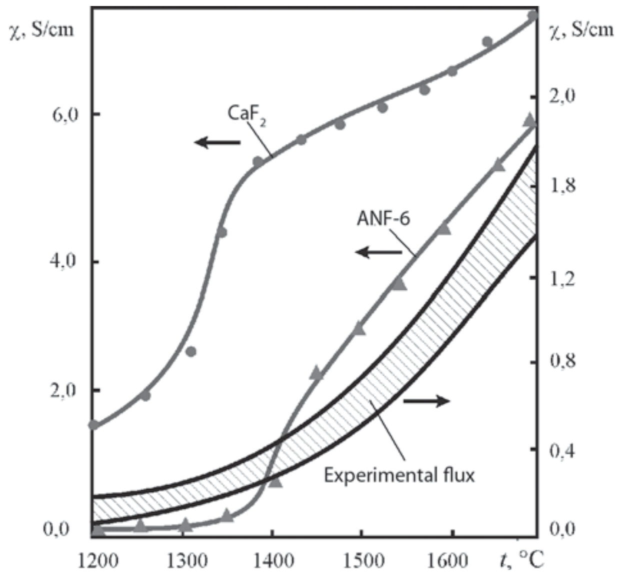

Fig. 1. The influence of temperature on electric conductivity of pure CaF_2, ANF-6 (to the left) and experimental flux (to the right)

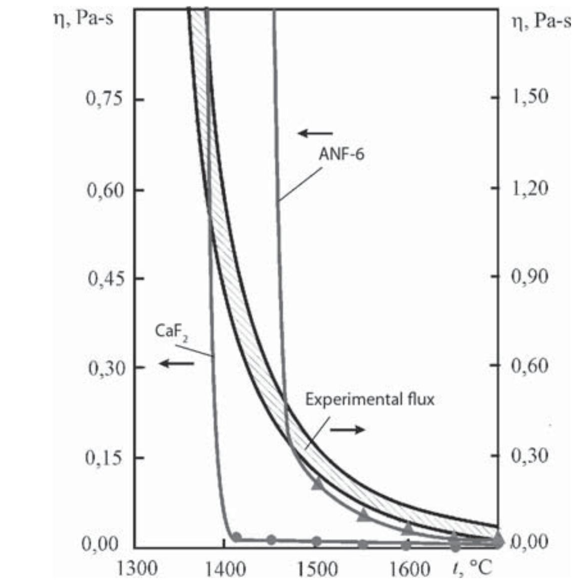

Fig. 2. The influence of temperature on viscosity of pure CaF_2 and ANF-6 (to the left) and experimental flux (to the right)

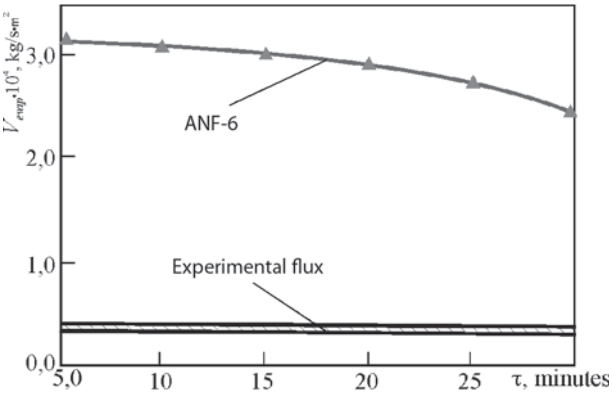

Fig. 3. Changing the rate of evaporation of the slag melt at ESR under the flux ANF-6 and experimental flux during the time

lic inclusions, mechanical properties were monitored. Quality control of the deformed metal was carried out in accordance with the requirements of GOST. We determined the chemical composition of the metal, the gas content in it, macrostructure, steel pollution by non-metallic inclusions, the size of the austenite grains, the mechanical properties of metal.

3. Results

The results of studies of the physical properties of experimental fluxes in relation to calcium fluoride flux ANF-6 are shown in **Fig. 1–3** and **Table 2**.

The melting point of experimental flux slightly lower than the melting temperature of the flux ANF-6, but meets the requirements for fluxes for the ESR of steel. In accordance with the phase diagram of oxides system CaO-SiO_2-Al_2O_3-MgO, the melting temperature of the flux is in the region, corresponding to melilite (which melting point is about 1300 to 1400 °C). The electrical conductivity of new flux is lower (fig. 1), but viscosity (fig. 2) is much higher than that of ANF-6. This is apparently, due to the fact that in the oxide-fluoride ANF-6 flux melt the basic structural units are small cations Ca^{2+}, Al^{3+}, anions O^{2-} and F^{2-}, but in the melt of experimental flux — the large slow-moving silicon-oxygen anions like $(SO_4)^{4-}$, $(Si_2O_7)^{6-}$ and so on. It is shown that experimental flux is a "long" or insignificantly changing viscosity and electrical conductivity over a wide temperature range. It does not crystallize on cooling, and solidifies to form a glass. It is known that the "long" fluxes have good forming ability, provide high quality surface of the ingot, which is especially important for remelting in the movable mold.

Flux ANF-6 is "short", or viscosity and the electrical conductivity of which change sharply in the temperature range 1400–1450 °C. Due to the lower electrical conductivity of the experimental flux compared with an electrical conductivity of the ANF-6 flux, electroslag remelting process under the experimental flux should proceed with greater speed and lower consumption of electric energy. The rate of evaporation of experimental flux by almost an order less than the flux ANF-6. This is occurred due to the fact that this flux by 70% consists

Table 2. Some physical properties of ESR fluxes

Flux	Melting point, °C	Evaporation speed at 1600 °C, $v \cdot 10^4$, kg/s·m²	Specific electric conductivity at 1600 °C, S·cm	Viscosity at 1600 °C, Pa·s
ANF-6	1437	2,5–3,1	4,1	0,1
Experimental*	1370	0,37	1,2	0,15
*) Experimental — using slags of ferroalloy production				

of CaF_2, which has a sufficiently high vapor pressure. In addition, the reaction

$$3CaF_2 + Al_2O_3 = 3CaO + 2AlF_3,$$

proceeds in the system CaF_2–Al_2O_3, in which AlF_3 is formed — a substance with high vapor pressure [5].

Technological properties of the experimental flux and flux ANF-6 were studied under laboratory conditions. It is established that experimental flux allows easy to start, steadily carry out the process of remelting and ensure obtaining ingots with a good surface quality. The scull on the surface of the ingots, melted under the experimental flux, is thinner and more uniform than it on the ingots, melted under the flux ANF-6. The productivity of the ESR process under experimental flux is almost by 1.5 times higher than for remelting under ANF-6 flux. Experimental flux does not contribute the purifying metal from the sulfur, oxygen level and amount of nonmetallic inclusions. Their quantity is larger in the melted metal than in the original. However, the inclusions have a favorable globular shape and their size is less than 5 microns.

Technological parameters of the ESR under experimental flux in industrial conditions are presented in **Table 3**. Regardless of the method of starting the ESR process (cold or hot start) and of the type of the ESR unit, the processes of bath initiating, metal refining and ingot pulling passed without difficulty and were very stable. Electric regime of remelting under the experimental fluxes was stable over a wide range of voltages (40–75 V). At the same time electricity consumption by remelting under experimental flux is almost by 1.5 times lower than under the standard fluxes ANF-6 and ANF-35 (24–30% CaF_2, 28–32% Al_2O_3, 20–26% CaO, 12–16% MgO, 4–8% SiO_2). The ingots welded under the experimental flux, have a clean and flat surface. Slag scull had a thickness of 0.2–2 mm.

The chemical composition of the initial and remelted for pipe billet steel (data from 11 billets) is shown in **Table 4**. It is showed, that the composition of the steel 38KhN3MFA (Ni–Cr–Mo steel, analogue of DIN 35NiCrMoV12-5) remelted under the proposed flux does not undergo significant changes and remains within the requirements of GOST.

Due to the low base-to-acid ratio of the experimental flux, the level of sulfur and phosphorus in the metal during remelting decreases insignificantly. However, the segregation of sulfur on Bauman's prints were not detected, which appearance is occurred due to changes in the distribution of sulfur in the ingot and in the conditions of the segregation of sulfide inclusions. Changing of the content of hydrogen in the metal during remelting is shown on **Fig. 4**.

Macrostructure of ingots, welded in industrial conditions under different fluxes and deformed billets, is sound and has no visible defects. On the fracture surfaces of transverse templates of ingots, deposited under ANF-6 flux, the boundaries between the crystallites having the form of cleavage surface are revealed. The fractures of templates of the ingots, welded under the experimental flux are transcrystalline, with no visible defects. This is

Table 3. Technological parameters of ESR at different units under various fluxes

Parameters	ESR unit / flux					
	ESHP – 0,25VG		ESHP–2,5VG– I1		R951	
	ANF-6	Experimental	ANF-6*	Experimental	ANF-35	Experimental
Current, A	2,9–3,2	2,1–2,5	8–10	7–8	10,8–12	10–12
Voltage, V	40–60	40–75	55–60	60–65	43–65	45–75
Remelting time, minutes.	42	30	375	274	355	210
Energy consumption per cycle, kW	107	66	3210	2140	3700	2400
Remelting rate, g/min	647	946	4267	5839	7155	11357
Ingot weight, t	27,2	28,4	1600	1600	2540	2385
Crystallizer size, mm	100	100	410 (with mandrel 150mm)	410 (with mandrel 150mm)	390–460	390–460

* — 10 % of SiO_2 were added for better forming

Table 4. Chemical composition of 38KhN3MFA steel before and after ESR

Steel	Chemical composition (mass %)									
	C	Mn	Si	P	S	Cr	Ni	Mo	V	O
Initial	0.33–0.39 / 0,37	0.28–0.60 / 0.46	0.24–0.37 / 0,29	0,010–0,025 / 0.018	0.015–0.023 / 0,020	1.20–1.42 / 1.29	3.05–3.16 / 3,10	0.35–0.45 / 0,39	0.10–0.15 / 0.13	0.0024–0.0026 / 0.0025
After ESR	0.33–0.37 / 0,34	0.25–0.50 / 0.39	0.18–0.37 / 0.28	0.0I0–0.020 / 0.014	0.010–0.022 / 0,016	1.20–1.4I / 1,27	3.04–3.33 / 3.16	0.36–0.44 / 0,39	0.10–0.18 / 0.14	0.0060–0.0095 / 0,0078
GOST 4543 Requirements	0.33–0.40	0.25–0.50	0.I7–0.37	<0,025	<0.025	I.20–1.50	3.00–3.50	0.35–0.45	0.I0–0.I8	—

Note: The numerator — the absolute values, the denominator — the average of 11 billets

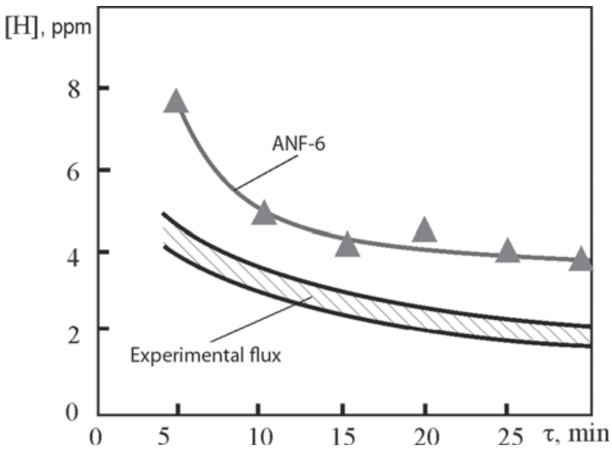

Fig. 4. Changing of the content of hydrogen in the metal during ESR

Table 5. Mechanical properties of cast and deformed steel 38HN3MFA, welded under the experimental flux in the stationary crystallizer

Type of metal	Mechanical properties				
	Flow limit, MPa	Rupture strength, MPa	Relative elongation, %	Relative reduction, %	KCU, KJ/m²
Cast	1387	1522	16,0	37,8	697
Forged (forging reduction — 2,2)	1404	1546	16,2	50,1	810
GOST 4543 requirements	1100	1200	12	50	800

Table 6. Mechanical properties of cast steel 38KhN3MFA after ESR in movable crystallizer

Flux	Mechanical properties				
	Flow limit, MPa	Rupture strength, MPa	Relative elongation, %	Relative reduction, %	KCU, KJ/m²
ANF-6	854	992	11,7	28,3	579
Experimental	884	1018	13,4	35,9	591

occurred, apparently, due to the different nature of formation of sulfides during the metal crystallization. When remelting under ANF-6, sulphides are located along the boundaries of the crystallites, while after remelting under experimental flux — on the surface of silica globules.

The 38KhN3MFA steel, melted under the experimental flux, at a sufficient level of strength properties characterized by high ductility and impact hardness, and ductility value close to the GOST requirements for deformed metal (see **Table 5** and **6**).

4. Discussion

As it follows from the experiments, flux, made from waste slag of ferroalloy production, is not inferior to the properties of flux, made of pure lime, quartzite, magnesite powder, technical alumina and fluorspar [3–4]. Experimental flux makes it easy to begin the process of ESR, to hold it in a stable mode, and provides a good surface of solid and hollow ingots. Remelting under experimental flux occurs at a higher speed and lower power consumption than remelting under the standard flux ANF-6, and provides much lower (2–4 ppm) hydrogen content in cast metal. Melting alloyed steel under the experimental flux does not cause undesirable changes in the content of alloying elements. At the same time melting under such fluxes cannot effectively refine the metal from sulfur and phosphorus and is accompanied by rising contamination of metal by oxide inclusions. However, changing the nature of nonmetallic inclusions, their shape, size and allocation of the sulfide phase in the form of shells on oxide inclusions favorably affects on the mechanical properties and fracture of cast metal.

Steel, remelted under experimental flux, is characterized by high rates of ductility and impact hardness.

5. Conclusions

Thus, the effective compositions of ESR fluxes, based on worked-out metallurgical slag, were proposed. The usage of such fluxes could solve three problems in metallurgy — increasing of efficiency of elecroslag remelting of steel, utilizing of worked-out ferroalloy slag and serious decreasing of emissions of poison compounds during ESR process.

REFERENCES

1. Dovgopol V. I. Ispolzovanie shlakov chernoy metallurgii (Use of steel slags). *Metallurgiya* = Metallurgy. Moscow. 1969. 216 p.
2. Bialucha R., Merkel T., Motz H. European environmental policy and its influence on the use of slag products. Proceedings of 2nd International Slag Valorisation Symposium. Leuven Apr. 18–20, 2011. P. 201–213.
3. Roshin V. E., Malkov N. V., Shvyrkunov V. V. Vyazkost i elektroprovodnost maloftoridnykh nizkoosnovnykh rasplavov tipa domennykh shlakov (Viscosity and electrical conductivity of low fluorine low bace-to-acid melts of the sort of blast furnace slags). *Spetsialnaya elektrometallurgiya* = Special electometallurgy. 1988. Vol. 66. P. 38–41.
4. Roshin V. E., Malkov N. V., Shvyrkunov V. V., Zakharov M. M., Tregubova T. G. Struktura i svoistva elektroshlakovogo metalla, pereplavlennogo pod flyusom domennykh shlakov (The structure and the properties of ESR metal, melted under the flux of blast furnace slags). *Spetsialnaya elektrometallurgiya* =Special electometallurgy. 1989. Vol. 67. P. 3–7.
5. Roshin V. E., Malkov N. V., Gainullin A. A., Zakharov M. M., Gribanov V. P. Kinetika ispareniya rasplavov CaF_2–SiO_2 s dobavkami oksidov redkozemelnykh metallov (The kinetic of evaporation CaF_2–SiO_2 melts with rare-earth metals additions). *Izvestiya RAN. Metally* = Proceedings of RAS. Metals. 1984. № 3, P. 56–61.