

This issue of journal contains scientific-technical papers and papers dedicated to industrial points, prepared by the specialists in the field of development, production and application of welding and surfacing consumables. Among the authors are the apprentices and followers of Prof. I.K. Pokhodnya, heads and specialists of a series of enterprises manufacturing welding consumables. Readers of the journal will also be able to familiarize with current market of welding consumables in Ukraine, examples of successful organization of production and realization of the products, recommendations on increase the competitiveness of domestic welding consumables.

Editorial note

EFFECT OF BINDER TYPE ON MANUFACTURABILITY AND PROPERTIES OF E-08Kh20N9G2B TYPE COATED ELECTRODES

K.A. YUSHCHENKO, A.V. BULAT, N.V. SKORINA, A.E. MARCHENKO, V.I. SAMOJLENKO and N.Yu. KAKHOVSKY

E.O. Paton Electric Welding Institute, NASU
11 Kazimir Malevich Str., 03680, Kiev, Ukraine. E-mail: office@paton.kiev.ua

The results of investigations of the properties of electrode compounds, coatings and electrodes of rutile-basic type were set forth and analyzed. These electrodes are designed for welding of high-strength Cr–Ni steels depending on composition of lithium-containing liquid glass. It is shown that application of Li–Na–K liquid glass for manufacture of such electrodes allows significantly improving their hygiene and sanitary properties due to reduction of specific emissions of hexavalent chromium high-toxic compounds. Simultaneously, application of Li–Na–K glass results in significant decrease of hygroscopic capacity of the coating, at that its strength and crack resistance in welding do not deteriorate, and ductility and impact toughness of weld metal is somewhat improved. The workability indices and welding-technological characteristics of compared electrodes are at the same level. The results of the investigations allowed upgrading coating composition and production technology of ANV-35 electrodes. 23 Ref., 9 Tables, 2 Figures.

Keywords: *high-alloy Cr–Ni steels, arc welding, coated electrodes, binders, processing characteristics of electrode compounds, strength and hygroscopic properties of electrode coatings, welding-technological and hygienic properties of electrodes, composition and structure of deposited metal, mechanical properties of weld metal*

In course of many decades the E.O. Paton Electric Welding Institute, carried out investigations under the leadership of Prof. I.K. Pokhodnya, academician of the NAS of Ukraine. They were directed on reduction of specific emissions and toxicity of the fumes, forming in welding using general designation electrodes. The main results are generalized in works [1, 2]. Under his guidance in 2013–2015 the studies were carried out on possibility of improvement of sanitary and hygiene characteristics of the general designation electrodes due to variation of types of applied binder.

Application of forced ventilation does not always help to remove the high-toxic compounds of hexavalent chromium (MAC 0.01 mg/m³) [3], contained in a welding fume (WF), from air of welder's working zone in manual arc welding of high-alloy Cr–Ni

steels. Besides, forced ventilation can not be used at all in performance of repair works inside capacitive and column equipment at the enterprises of petrochemical and chemical industry.

Experimental investigations determined a mutagenic nature of WF containing hexavalent chromium compounds. Therefore, now exceptionally large attention in the world is given to improvement of sanitary and hygiene properties of the electrodes designed for welding of high-alloy Cr–Ni steels. A successful solution of this problem, undoubtedly, depends on knowledge of fundamental characteristics as well as conditions of WF formation in welding of indicated steels.

It follows from domestic and foreign publications [4–9] that:

- chromium (the second after manganese metal on value of vapor pressure at arc welding process tem-

*The work was carried out by initiative of Prof. I.K. Pokhodnya, academician of the NAS of Ukraine. Engineers O.I. Folbort and A.I. Radchenko participated in the work.

peratures) transfers to a welding fume solid constituent (WFSC) from the electrode and base metal as well as metallic constituents of electrode coating;

- intensity of transfer and valence of chromium in WFSC depend on its content in melted metal and electrode, real composition of slag-forming part of the coating and slag forming from it. The higher chromium content in steel and, respectively, in welding consumable, the more chromium is in WFSC. Following from the acting sanitary norms, a danger of chromium emission should be taken into account in welding of steels containing more than 5 % of chromium. Fluxing materials, as a rule, restrain chromium evaporation. Therefore, other conditions being equal, total content of chromium in WFSC in shielded-gas welding, even at high oxidizing capacity, is higher than in coated electrode welding. At that no hexavalent modification of chromium was found in it;

- according to existing classification chromium compounds in WF are divided on soluble and insoluble in water. Each of mentioned modifications includes compounds from three- or hexavalent chromium. Total portion of chromium in WFSC during coated electrode welding for stainless steels joining varies from 3 to 7 % among them from 60 to 90 % falls at its soluble compounds, representing themselves, as a rule, potassium and sodium chromates;

- the largest levels of emission of hexavalent chromium compounds in welder breath zone are observed when using the electrodes with basic coating, they are lower for rutile-basic electrodes and rutile-coated electrodes have the lowest emissions. There is no one-valued relationship between the total level of WFSC emission and content of hexavalent chromium in it. The first is related with arc voltage (power) and gas-forming capacity of the coating, the second with its oxidizing capability;

- instrumental methods proved that chromate (soluble) form of hexavalent chromium compound in the welding fume is caused by potassium and sodium silicates, being a constituent of the electrode coating or flux-cored wire core. A source of entering of alkali oxides, i.e. liquid glass, fluor spar or mica in the coating has no matter. The soluble compounds of hexavalent chromium are not detected in WFSC during welding using electrodes with lithium silicate;

- role of CaF_2 in formation of the hexavalent chromium compounds is not investigated, however there is certain correlation between emission of hexavalent chromium and soluble fluorides. Reduction of $\text{CaCO}_3/\text{CaF}_2$ relationship in the electrode coating results in increase of fume emission and content in it of Cr^{+6} compounds. Moreover, potassium chromates in WFSC were found in welding using electrodes having no CaF_2 in their coating;

- electrodes, which are made based on lithium silicate for complete suppression of Cr^{+6} , show a series of sufficiently significant process and service disadvantages. In particular, arc burning stability is substantially deteriorated and as a result such electrodes can not be used for alternating current welding. Coating strength is dramatically reduced, it cracks in welding that results in worsening of protection of molten metal from environment. Based on foreign publications, indicated disadvantages of the electrodes can be eliminated by means of improvement of coating composition and adjustment of process parameters of their manufacture. Necessary lithium-containing liquid glasses [10, 11] as well as new electrode grades are developed and manufactured. However, the electrodes with improved sanitary and hygiene indices, which guarantee the requirements of commercial consumer, have not appear yet at the market.

Aim of the following work lies in the following:

- determination of a way for reduction of Cr^{+6} emission in WF due to process means of electrode manufacture, including determination of optimum relationship of lithium-sodium-potassium compounds in liquid glass binder, at which no changes in electrodes and welding process indices take place;

- specification of a role of coating constituents, in particular, CaF_2 in formation of Cr^{+6} compounds in WFSC content.

Object and experimental procedures. Electrodes of ANV-35 (E-08Kh20N9G2B on GOST 10051-75) with rutile-basic coating were investigated. Materials corresponding to the requirements of reference documents on composition and grain-size were used for manufacture. Rod diameter is 3 mm, coating is 4.95–5.15 mm and 350 mm length. Table 1 shows the composition and characteristics of liquid glasses selected

Table 1. Composition (wt.%) and characteristics of liquid glasses

| Type of liquid glass | Silicate module, rel. un. | SiO_2 | Li_2O | Na_2O | K_2O | D.r.* | Density, g/cm^3 / toughness, MPa·s |
|----------------------|---------------------------|----------------|-----------------------|-----------------------|----------------------|-------|--|
| K–Na | 2.88 | 27.85 | – | 3.90 | 9.25 | 41.00 | 1.43/590 |
| Li–Na–K | 2.19 | 27.75 | 1.80 | 7.00 | 3.60 | 40.15 | 1.38/530 |
| Li–Na | 2.75 | 30.20 | 2.70 | 5.17 | 1.00 | 39.07 | 1.39/525 |
| Li | 3.60 | 22.80 | 3.15 | – | – | 25.95 | 1.25/535 |

*D.r. — dry residual of liquid glass.

for planned experiments in course of preliminary experiments.

Since lithium silicates are not soluble in water, their aqueous solutions were synthetically produced by means of chemical reaction of taken in necessary relationship aqueous solution of lithium hydrate with powder of aqua silicon acid at 50–60 °C temperature. Brought up to set characteristics, they were mixed with Na and K–Na liquid glasses, produced using autoclave solving of corresponding silicate rocks.

Electrode compounds were prepared in an intensive mixer in course of 3 min. Their properties were evaluated on plastic strength P_m value, characterizing hardness of electrode compound in state of briquette and coating just applied on a rod as well as value and uniformity of flow pressure P_e through die hole of 4 mm diameter and 40 mm length. Mentioned indices were evaluated using cone aotoplastometer OB2059 and capillary viscometer OB1435, developed and manufactured at the E.O. Paton Electric Welding Institute. The procedures are described in work [12].

At that it was assumed that the coating, which is characterized by higher ductility strength at the same pressure, has the best properties.

Strength of dewatered coating of the electrodes was determined using three-point bend method of cylinder samples of 4 mm diameter and 50 mm length, made by means of extrusion of compound mass [13]. Dewatering of the samples was carried out through their drying-baking at 200, 300, 350 and 400 °C during one hour.

Hygroscopy of the coating was evaluated on kinetics of moisture sorption at short-term (8 hours) and long-term (2 weeks) exposure of the electrode samples in hydrostat at 20 °C and relative air humidity 84 %. Amount of absorbed moisture was determined by weighing of the samples with 1 and 24 hours time gap; mass increment was related to dry coating mass.

Comparative evaluation of binder effect on coating crack resistance in welding was determined using the following procedure. Welding using experimental electrodes was carried out from VDU-504 rectifier using reverse polarity ($I_w = 90–100$ A). For each variant at least three experiments were performed by means of continuous fusion of electrodes of 350 mm length to stub of 50, 130 and 200 mm length. After cooling to room temperature the coating surface of each stub was examined and amount and length of cracks were determined in accordance with the requirements of GOST 9466–75, i.3. If no rejection signs were found, coating resistance to chips was evaluated by means of stub drop on a steel plate from 0.5 m height. The chips of any size on working part of the coating of the

tested sample (except for stub of 50 mm length) are not permitted.

Welding-technological properties of the electrodes were compared in terms of arc burning stability, weld formation quality and separation of slag crust, which were determined in welding and surfacing on plates of 12Kh18N10T steel using reverse polarity direct current from VDU 504 ($U_{o-c} = 80$ V) rectifier.

Arc burning stability was estimated by standard deviations of current and arc voltage (σ_{I_a} and σ_{U_a}) from statistically average indices (I_a^{av} and U_a^{av}). They were received with the help of introduced in a welding circuit nonstationary processes analyzer of ANP-2 type [14], allowing in a real time mode reading, storing and statistically processing digital information on current and voltage changes.

Quality of metal formation was evaluated on the average values of weld geometry coefficient K_g^{av} , representing itself a relationship of weld width to its height [15]. Corresponding measurements were carried out on the beads deposited with pilot electrodes on plate surface in flat, vertical and overhead positions with transverse 7–8 mm amplitude oscillations of the electrodes.

Separation of a slag crust was determined following procedure [16] on ϕ_{av}^0 index, representing itself average value of enforced vee angle of plates butt joint, at which the slag crust is completely separated from a root weld surface.

Effect of binder type on composition and structure of deposited metal as well as mechanical properties of weld metal was evaluated in accordance with the requirements of GOST 9466–75. For this eight-layer deposits were made by experimental electrodes, in which content of C, Cr, Ni, Mn, Nb, S and P was determined by method of diffusion spectrometry (spectrometer DFS-51), and content of α -phase (δ -ferrite) was determined by magnetometer method (magnetometer MF-10I). Nine cylinder samples of 5 mm diameter and length were cut from upper layers for determination of content of oxygen, hydrogen and nitrogen. Analysis was carried out on LECORO-316, LECOPH-402 and LECOTN-114 units by reduction melting method [17].

Mechanical properties of weld metal were evaluated in accordance with GOST 9466–75. For this butt joints of plates of 12Kh18N10T steel were welded using the experimental electrodes. Welding was made using reverse polarity direct current ($I_w = 80–90$ A) from VDU 504 rectifier. Three samples of II and IX type on GOST 6996–66 were cut out from the indicated joints for static tension and impact bend test, respectively. Yield strength, strength and relative elon-

Table 2. Process characteristics of electrode compounds (nature of flow — uniform)

| Binder | | Plastic strength P_m , MPa | Extrusion indices | |
|---------|---------|------------------------------|--|------|
| Type | Dose, % | | Pressure P_e , MPa in consumption Q , cm ³ /s | |
| | | | 1 | 10 |
| K-Na | 23.1 | 0.25 | 32.5 | 37.0 |
| Li-Na-K | 24.0 | 0.72 | 33.5 | 35.5 |
| Li-Na | 24.0 | 0.75 | 34.0 | 42.5 |
| Li | 25.7 | 0.90 | 18.5 | 21.0 |

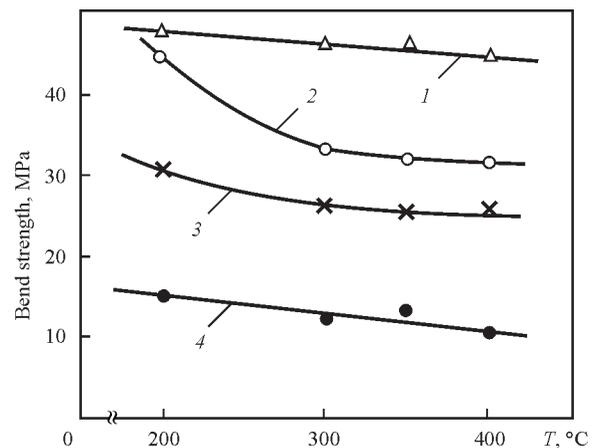
gation (σ_y , σ_t and δ_5) as well as impact toughness were determined on sharp notch samples (*KCV*).

Composition of slags was determined by X-ray spectrum analysis method using X'Unique II Philips device, and specific emissions of WFSC were found by total filtration method (three experiments for each variant of the electrodes). The filters from Petryanov tissue of FPP15-1.5 grade [16] were used. WFSC samples were precipitated on AFA-KhA-18 filters [17–19] for chemical analysis. All experiments were carried out in special chamber under similar conditions in reverse polarity direct current surfacing ($I_w = 90\text{--}100\text{A}$) on plates of steel 12Kh18N10T.

Investigation results. Results of evaluation of process indices of the electrode compounds are given in Table 2.

It can be seen that lithium-containing binders provide for higher ductility of electrode compound in comparison with potassium-sodium liquid glass, which is usually used for manufacture of ANV-35 electrodes. It becomes apparent due to almost three-fold increase of their plastic strength at equivalent extrusion pressure.

The results of coating strength tests are given in Figure 1. It can be seen that independent on binder

**Figure 1.** Effect of type of liquid glass and baking temperature on results of testing of coating bend strength: 1 — K-Na; 2 — Li-Na-K; 3 — Li-Na; 4 — Li

type increase of sample baking temperature results in decrease of their strength. K-Na liquid glass provides for maximum coating strength. It reduces by 11, 22 and 80 %, respectively, using Li-Na-K, Li-Na and Li types of binders. In the case of Li-Na-K and Li-Na binders, the strength reduction level is not critical in contrast to the samples, manufactured based on lithium binder.

The results of comparison of hygroscopic characteristics of the coatings, produced using different liquid glasses, are given in Figure 2.

It can be seen that in comparison with standard K-Na liquid glass the lithium-containing binder provides for lower (6–8 times) hygroscopy of the electrode coating. In this connection they have small difference from pure lithium binder. Such an effect is apparently related with compression of silicon-oxygen mesh at implantation in it of lithium ions and agrees with known virtually complete incapability of lithium ions to hydration.

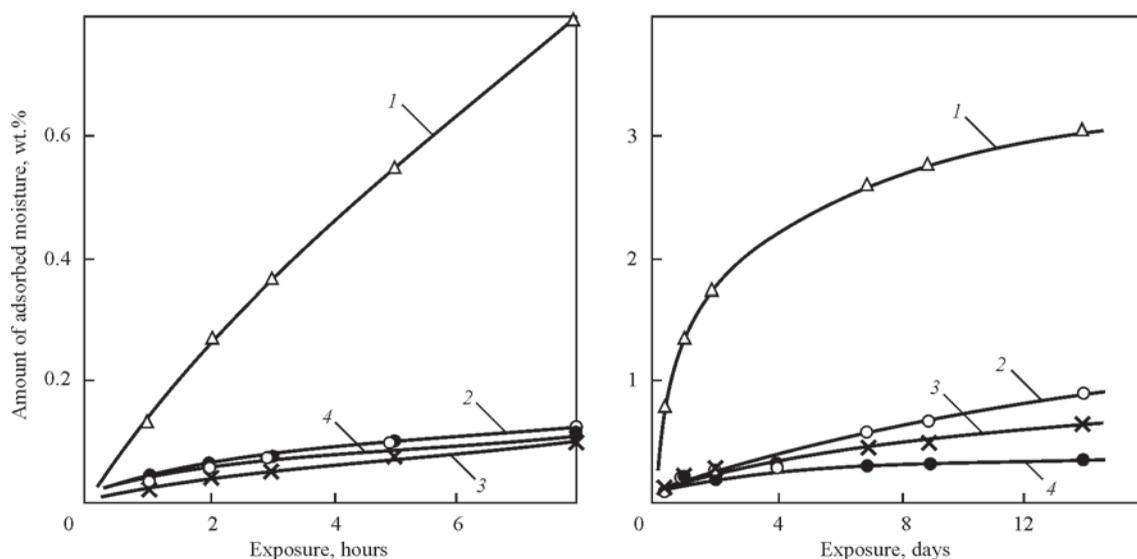
**Figure 2.** Effect of binder type on kinetics of sorption of atmospheric moisture by electrode coatings (designations are the same as in Figure 1)

Table 3. Effect of binder type on electrode coating susceptibility to crack in welding

| Binder type | Diameters of electrode/coating, mm | Length of stub, mm | Average length of cracks, formed in electrode coating from | | Nature of coating cracking |
|-------------|------------------------------------|--------------------|--|-----------------|---|
| | | | bushing, mm | contact end, mm | |
| K–Na | 3.0/5.00 | 60 | – | – | Cracks are formed in 50–60 s after welding completion |
| | | 136 | – | 25 | |
| | | 225 | 27 | 30 | |
| Li–Na–K | 3.0/5.05 | 62 | – | – | |
| | | 134 | 5 | 27 | |
| | | 222 | 30 | 38 | |
| Li–Na | 3.0/4.95 | 64 | – | 20 | Cracks are formed during welding and propagate after its completion |
| | | 135 | 34 | 27 | |
| | | 223 | 35 | 40 | |
| Li | 3.0/5.15 | 64 | – | – | Excessive brittleness of coating before, during and after welding |
| | | 135 | – | – | |
| | | 227 | – | – | |

Table 4. Welding-technological properties of electrodes

| Type of liquid glass | Weld geometry coefficient K_g^{av} in surfacing in positions | | | Separability of slag crust ϕ_{av}^0 | Statistical characteristics of welding mode | | | |
|----------------------|--|----------|----------|--|---|--------------------|----------------|--------------------|
| | flat | vertical | overhead | | I_a^{av} , A | σ_{I_a} , A | U_a^{av} , V | σ_{U_a} , V |
| K–Na | 3.1 | 2.8 | 2.6 | 4 | 96.5 | 14.5 | 20.3 | 4.0 |
| Li–Na–K | 3.1 | 2.8 | 2.5 | 5 | 96.0 | 14.5 | 21.0 | 4.1 |
| Li–Na | 3.2 | 2.6 | 2.5 | 6 | 95.2 | 14.8 | 22.0 | 4.2 |
| Li | 2.8 | 2.5 | 2.3 | 8 | 94.3 | 18.2 | 23.5 | 5.7 |

Table 5. Composition (wt.%) and structure of deposited metal

| Type of liquid glass | C | Cr | Ni | Mn | Si | Nb | S | P | α -phase, % |
|-------------------------------|-----------|-------|----------|---------|------|---------|--------|--------|--------------------|
| K–Na | 0.053 | 20.1 | 10.2 | 1.3 | 1.0 | 0.7 | 0.011 | 0.022 | 7.5 |
| Li–Na–K | 0.053 | 19.6 | 9.9 | 1.3 | 1.1 | 0.7 | 0.010 | 0.021 | 6.5 |
| Li–Na | 0.051 | 19.9 | 10.1 | 1.3 | 1.0 | 0.7 | 0.010 | 0.022 | 6 |
| Li | 0.048 | 19.5 | 9.3 | 1.2 | 1.0 | 0.7 | 0.011 | 0.028 | 6 |
| Requirements of GOST 10052–75 | 0.05–0.12 | 18–22 | 8.0–10.5 | 1.0–2.5 | <1.3 | 0.7–1.3 | <0.020 | <0.030 | 2–8 |

Table 3 shows the results of testing of pilot electrode coating susceptibility to cracking. According to Table 3 allowable (from point of view of welding quality) susceptibility of the electrode coating to cracking is provided in use of K–Na and Li–Na–K binders. Application of Li–Na binder is unacceptable due to coating cracking in welding, and Li glass due to its excessive brittleness. It is necessary to pay attention on correlation of received results to coating strength values given in Figure 1.

Table 4 gives the indices of welding-technological properties of the electrodes. Based on them, variation of composition of the combined liquid glasses (K–Na, Li–Na–K or Na–Li) does not influence weld geometry coefficient in any welding position (difference of K_g^{av} values does not exceed 7 %).

Statistical indices of mode parameters of arc burning varies at that more systematically. Thus, increase of mass portion of lithium in the liquid glass (from 0 to 2.7 %) promotes for rise of statistically average values of voltage (from 20.3 to 22.0 V) and reduces that of current (from 96.5 to 95.2 A), while standard

deviations of current σ_{I_a} as well as σ_{U_a} at that rise from 14.5 to 14.8 and from 4.0 to 4.2 V, respectively. Nevertheless, variations of these indices do not exceed the 8 % limits that agree with the conclusions made in work [20]. Unfavorable effect of lithium, in particular on indices of arc voltage dissipation, can be considered critical only in the case of complete absence of Na_2O and K_2O in liquid glass.

Effect of liquid glass composition on slag crust separation is more noticeable. If the study is limited only with investigation of lithium-containing liquid glasses, than a separation index deteriorates with rise 1.5 time of lithium portion in liquid glass; if we take into account the results of testing of the electrodes produced only based on pure lithium glass, this index degrades 2 times.

The results of testing of chemical composition and metal structure deposited with experimental electrodes are given in Table 5, content of gases is in Table 6 and weld metal mechanical properties in Table 7. All electrodes on chemical composition and content

of α -phase are virtually similar and correspond to E-08Kh20N9G2B type on GOST 10052–75. Moreover, it is determined that application of Li-containing binders results in decrease in the deposited metal of oxygen and hydrogen content and rise of nitrogen. In our opinion it is caused by increase of reduction capacity of the slags.

The average (from three results) values of mechanical properties indices of weld metal are given in Table 7. According to received data application of Li-containing binders instead of standard K–Na liquid glass allows significantly increasing relative elongation and impact toughness of weld metal that can be explained by decrease of oxygen content and rise of nitrogen in it (see Table 6).

Composition of the slags and experimental electrodes are given in Table 8. It follows from it that composition of welding slag to sufficient extent depends on type of liquid glass. The largest deviations lied in the following:

- five-fold decrease of K_2O portion in the slag at transfer from K–Na to Li-liquid glass (it is promoted, from one side, by reduction of K_2O portion in the liquid glass and, at the same time, K_2O evaporation);

Table 7. Mechanical properties of weld metal (temperature 20 °C)

| Type of liquid glass | σ_y , MPa | Σ , MPa | δ_s , % | KCU, J/cm ² | KCV, J/cm ² |
|-------------------------------|------------------|----------------|----------------|------------------------|------------------------|
| K–Na | 567.1 | 709.5 | 29.5 | – | 88.5 |
| Li–Na–K | 513.7 | 702.9 | 35.3 | – | 117.7 |
| Li–Na | 535.0 | 713.1 | 33.3 | – | 129.3 |
| Li | 507.3 | 708.2 | 38.5 | – | 122.3 |
| Requirements of GOST 10052–75 | Not regulated | >55 | >22 | >8.0 | Not regulated |

Table 8. Composition of slags (wt.%)

| Type of liquid glass | TiO ₂ | SiO ₂ | CaO | MgO | MnO | Fe ₂ O ₃ | Al ₂ O ₃ | Cr ₂ O ₃ | Nb ₂ O ₅ | Na ₂ O | K ₂ O | CaF ₂ |
|----------------------|------------------|------------------|------|-----|-----|--------------------------------|--------------------------------|--------------------------------|--------------------------------|-------------------|------------------|------------------|
| K–Na (0) | 30.9 | 16.1 | 15.3 | 1.1 | 5.4 | 1.6 | 5.4 | 7.1 | 1.9 | 1.0 | 2.5 | 11.2 |
| Li–Na–K(1.80) | 30.8 | 16.5 | 14.5 | 1.3 | 5.6 | 1.6 | 5.6 | 7.0 | 1.9 | 1.0 | 1.3 | 12.7 |
| Li–Na(2.70) | 30.0 | 16.7 | 11.5 | 1.6 | 5.3 | 1.1 | 5.4 | 7.5 | 1.8 | 1.9 | 0.8 | 16.1 |
| Li(3.15) | 31.3 | 16.1 | 10.9 | 1.4 | 5.5 | 1.6 | 5.4 | 7.1 | 1.9 | – | 0.5 | 17.9 |

Note. Portion of Li₂O is indicated in the brackets. Portion of V₂O₅ – 0.1 %, ZrO₂ – 0.4 %. Fraction relationship of chromium oxides in slags was not determined.

Table 9. Indices of emission and composition of WFSC

| Type of liquid glass | WFSC total emission | | Weight fraction, % in WFSC | | | | | |
|----------------------|-------------------------|-----------------------|----------------------------|------------------|------|------|----------------|-----------------|
| | Intensity V_a , g/min | Specific G_a , g/kg | Cr ⁶⁺ | Cr ³⁺ | Mn | Ni | F _p | F _{np} |
| K–Na (0 %) | 0.50 | 11.58 | 1.96 | 2.62 | 4.81 | 1.47 | 11.68 | 1.30 |
| Li–Na–K (0.7 %) | 0.45 | 10.10 | 1.77 | 2.67 | 5.27 | 1.38 | 10.24 | 1.69 |
| Li–Na–K (1.8 %) | 0.35 | 7.28 | 1.44 | 2.82 | 5.69 | 1.29 | 10.35 | 1.88 |
| Li–Na (2.7 %) | 0.26 | 5.52 | 0.89 | 3.04 | 5.73 | 1.62 | 11.65 | 1.34 |
| Li (3.2 %*) | 0.20 | 4.52 | Not detected | 3.91 | 5.20 | 1.39 | 5.76 | 1.56 |

Note. Weight portion of Li₂O in liquid glass is indicated in the brackets.

Table 6. Content of gases in deposited metal, wt.%

| Type of liquid glass | H | N | O |
|----------------------|--------|-------|-------|
| K–Na | 0.0015 | 0.067 | 0.062 |
| Li–Na–K | 0.0014 | 0.072 | 0.058 |
| Li–Na | 0.0012 | 0.079 | 0.051 |
| Li | 0.0010 | 0.082 | 0.045 |

- 1.6 time rise of CaF₂ portion in slag that, undoubtedly, related with decrease of escape of fluorine at transfer from K–Na to Li liquid glass;

- 1.4 time reduction of CaO portion.

The rest of constituents, including portion of Cr₂O₃, was kept at the same level.

Table 9 generalizes the results of testing the sanitary and hygiene characteristics of the experimental electrodes. Another set of liquid glasses was used for their manufacture.

It can be seen that application of lithium-containing binders instead of K–Na liquid glass significantly improves sanitary and hygiene indices of the electrodes. It reveals through reduction of WFSC emission and content in the fume of the most hazardous constituent, namely hexavalent chromium. The level of improvement of sanitary and hygiene indices rises with increase of a portion of lithium constituent in the liquid glass. The largest effect is reached in ap-

plication of Li–Na and Li-silicates. In comparison with K–Na analogue WFSC specific emission and its intensity reduces 2 times for Li–Na and 2.5 times for pure Li-silicate. Content of carcinogenic hexavalent chromium drops 2.2 times, and it is not revealed in WFSC at application of pure Li-binders.

Changes of slag material composition, in particular, rise of portion of CaF_2 and equivalent decrease of CaO portion at transfer from K–Na to Li liquid glasses are accompanied by intensive Cr^{+6} emission in WF content.

Let's consider given results in more details. Titanous slags are characterized by special physical-chemical properties. They are formed by low titanium oxides of different valence, capable to include in their structure a large number of oxides in liquid and solid states with close parameters of crystalline lattice (FeO , MnO , MgO , NiO , V_2O_5 , Cr_2O_3 , Al_2O_3), except for CaO, which forms perovskite with TiO_2 , sufficiently refractory compound, and SiO_2 , which is related with appearance of X-ray amorphous glass-like phase [21] in titanous (including welding) slags. Therefore, solidified titanous slags, even having significant difference between themselves on chemical composition, can be very similar to each other on crystalline lattice. In contrast to other welding slags they are characterized by low oxidizing capacity, and electrodes with rutile coating, designed for welding of low-carbon and low-alloy steels, are characterized by the highest sanitary and hygiene properties.

Lithium liquid glass intensifies reducing capability of titanium slags, since, based on current ideas, structure of lithium silicates does not have so called free oxygen. All oxygen is bounded with silicon atoms by strong siloxan linkages, and structure of the melt is characterized by the highest connectivity index (Q-factor) Q^4 [22]. Presence of K- and Na-oxides and CaF_2 in the rutile-basic type coating significantly complicates this picture, in general, suppressing favorable effect of low titanium and lithium oxides on sanitary and hygiene characteristics of the electrons.

Sodium and, in particular, potassium oxides evaporate easier from molten welding slags than lithium oxides. It can be explained through comparison of the coefficients of surface tension of alkali lithium, sodium and potassium silicates. Based on data of work [23] surface tension of $\text{Li}_2\text{O}\cdot\text{SiO}_2$ melt (315 MJ/cm^2) is significantly more than of $\text{Na}_2\text{O}\cdot\text{SiO}_2$ and $\text{K}_2\text{O}\cdot\text{SiO}_2$ melts (288 and 236 MJ/cm^2 , respectively). It is without doubt that $\text{Li}_2\text{O}\cdot\text{SiO}_2$ melt with larger surface tension will evaporate less intensively, than that of sodium and potassium silicates. Alkali oxides react with CaF_2 , form volatile soluble fluorides and enrich the melt with calcium oxide. The latter forms with tita-

um oxide the perovskite, weakening the melt by titanium sesqui oxides and, thus, decreasing its reducing capacity. This, in turn, simplifies formation of ions of hexavalent chromium. To the smallest extent this scheme is realized in slags of the electrodes produced based on lithium liquid glass, and it is proved by slag compositions given in Table 8.

Carried investigations allowed correcting basic composition of ANV-35 electrode coating mainly by means of limitation in it of portion of potassium, sodium and calcium oxides and application of Li–Na–K liquid glass. Upgraded ANV-35MK electrodes significantly exceeds ANV-35 electrodes on set of characteristics, including hygienic ones.

Conclusions

1. Effect of lithium-containing liquid glass on manufacturability, welding-technological properties of the electrodes, composition of deposited metal and mechanical properties of weld metal was studied by example of rutile-basic coated electrodes of E-08Kh20N9G2B type. It is determined that the optimum complex of technological and welding characteristics of the electrodes is provided by application of Li–Na–K binder with 1.5 % lithium constituent.

2. Application of Li–Na–K binder instead of K–Na liquid glass allows approximately 2 times reduction of emission of high-toxic Cr^{+6} compounds in WFSC composition, 7–8 times decrease of hygroscopy of electrode coating, 17 % rise of relative elongation and 30 % of weld metal impact toughness. At that, process indices and welding-technological properties of the electrodes remain unchanged.

3. Favorable effect of lithium oxides on decrease of emission of Cr^{+6} compounds in WF composition is caused by rise of slag reducing capacity due to blocking the processes of formation of potassium and sodium fluorides as well as potassium titanites.

4. Unfavorable effect of CaF_2 from point of view of emission of hexavalent chromium ions is explained by the fact that reaction of potassium fluoride formation is accompanied by increase of CaO in the slag, i.e. its basicity index. This results in increase of free oxygen in the slag. At the same time, rise of CaO portion in the slag provides for decrease of reducing capacity of the slag also because larger portion of higher titanium oxides coordinates with CaO (it is proved by perovskite formation in the solidified slag), while portion of low-valent titanium oxides, characterized by lower oxidizing capacity, equivalently reduces at that.

5. Coating composition of ANV-35 grade electrodes was upgraded with a view of application of Li–Na–K binder. New modifications of the electrodes was coded as ANV-35MK. They significantly exceed

the electrodes with basic coatings on set of characteristics, including hygiene one.

1. Pokhodnya, I.K., Gorpenyuk, V.N., Milichenko, S.S. et al. (1990) *Metallurgy of arc welding: processes in arc and melting of electrodes*. Kiev: Naukova Dumka.
2. Pokhodnya, I.K., Yavdoshchin, I.R., Gubunya, I.P. (2011) Welding fume – factors of influence, physical properties and methods of analysis (Review). *The Paton Welding J.*, **6**, 33–36.
3. *GOST 12.1.007–76 SS BT*: Harmful substances. Classification and general safety requirements. Introd. 01.01.1977.
4. Yushchenko, K.A., Levchenko, O.G., Bulat, A.V. et al. (2007) Sanitary and hygienic characteristics of covered electrodes for welding high-alloy steels. *The Paton Welding J.*, **12**, 35–38.
5. Levchenko, O.G., Bulat, A.V., Bezushko, O.M. (2010) Influence of electrode coating on hygienic characteristics of fumes, formed in welding of high-alloy steels. *Visnyk NT UU KPI. Seriya Girnystvo*, Issue 19, 171–177.
6. Kawada, K., Kobayashi, M. Experimental investigations on hazard of lithium in welding fume. *IIW Doc. VIII-286–79*.
7. Kimura, I., Kobayashi, M., Godai, T. et al. (1979) Investigations on chromium in stainless steel welding fume. *Welding Res. Suppl.*, **8**, 195–204.
8. Astrom, H. (1993) Advanced development techniques for coated electrodes. *Welding Rev. Int.*, **12(2)**, 72, 74, 76.
9. Griffiths, T., Stevenson, A. (1989) Binder developments for stainless electrodes. *Welding Rev.*, **8(3)**, 192, 194, 196.
10. *Inobond*. Special silicates for welding consumables. Company brochure Van Baerle, Switzerland.
11. CristalTME. A new generation of stainless steel MMA electrodes. Company brochure AirLiquide/Oerlikon.
12. Marchenko, A.E. (1978) About rheological methods for evaluation of technological properties of electrode compounds. Information of CMEA. *Coordination Center on problems: Development of scientific basics and new technological processes of welding, surfacing and thermal cutting of materials and alloys for manufacturing of welded structures and development of efficient welding consumables and equipment*, Issue 1(**13**), 121–128.
13. Marchenko, A.E. (2010) On physical-chemical nature of strength of electrode coatings and technological means of its ensuring. In: *Proc. of 5th Int. Conf. on Welding Consumables, Technologies, Manufacturing, Quality and Competitiveness* (Artyomovsk–Kiev, Ukraine, 2010), 78–99.
14. Pokhodnya, I.K., Ofengenden, R.G., Gorpenyuk, V.N. et al. (1979) Information-measuring system for investigation of technological properties of welding consumables, equipment and processes. *Avtomatich. Svarka*, **10**, 67–68.
15. Sidlin, Z.A., Tarlinsky, V.D. (1984) *Current types of coated electrodes and their application for arc welding*. Moscow: Mashinostroenie.
16. Lipodaev, V.N., Bojko, Yu.N., Kakhovsky, Yu.N. et al. *Method of evaluation of slag crust detachability*. USSR author's cert. 407689. Publ. 28.08.1973.
17. Kalinyuk, V.V. (2011) Organizing of analysis process for titanium alloys on oxygen, nitrogen, hydrogen and carbon content. *Metrologiya ta Prylady*, **2**, 50.
18. *MU 1927–78*: Guidelines. Hygienic evaluation of welding consumables and methods of welding, surfacing and cutting of metals. Moscow: Minzdrav SSSR, 1980.
19. *MU 4945–88*: Guidelines on determination of harmful substances in welding fume (solid phase and gases). Minzdrav SSSR, 1990.
20. Slania, J., Slazak, B. (2006) Badania porownawcze elektrod otulonych wysokostopowych ERWS 19-9 L productowanych przy zastosowaniu nowego szkła wodnego modyfikowanego tlenkiem litu. *Biul. Instytutu Spawalnictwa*, **6**, 48–53.
21. Rudneva, A.V., Model, M.S. (1963) Phase transformations during reduction of titanium dioxide in slag systems. *Izvestiya AN SSSR. Metallurgiya i Gornoe Delo*, **1**, 59.
22. Marchenko, A.E., Skorina, N.V., Kiselev, M.O. (2010) Evolution of concept on nature and properties of liquid glass, being important in manufacture of welding electrodes. In: *Proc. of Int. Conf. on Welding Consumables: Technologies, Manufacturing, Quality, Competitiveness* (Agoj, 7–10 June 2010). Kiev: PWI, 2010, 100–106.
23. Perminov, A.A., Popel, S.I., Smirnov, N.S. (1961) Influence of replacement of nitrogen oxide by oxides of other metals on surface tension of silicate melts and their adhesion to hard steel. *Izvestiya Vuzov. Chyorn. Metallurgiya*, **12**, 5–8.

Received 04.07.2016