


UDC 669.182.2:621.365.2

DOI: http://dx.doi.org/10.17580/cisisr.2017.02.02

IMPROVEMENT OF THE MELTING TECHNOLOGY AND LADLE TREATMENT OF STEELS 15X2HMФА(15Kh2NMFA) (A-A, CLASS 1) FOR SPECIAL CRITICAL DUTY COMPONENTS IN NUCLEAR POWER STATIONS

Dub V. A.1, Novikov S. V.2, Shchepkin I. A.2, Kornienko O. Yu.3

1 National University of Science and Technology “MISIS” (Moscow, Russia)
2 RF State Research Centre JSC SPA “CNIITMASH” (Moscow, Russia)
3 Ural State Federal University n. a. the 1st RF President B. N. Eltson (Ekaterinburg, Russia)

E-mail: o.j.kornienko@urfu.ru

AUTHOR'S INFO

V. A. Dub, Cand. Eng., Leading Expert, the Chair of Physical Chemistry.

ABSTRACT

The ways of increase of the power engineering products resource for large-size critical components made of steel 15Kh2NMFA are described in terms of radiation and thermal brittleness criteria due to the content restriction of harmful and impurity elements, primarily phosphorus, sulfur and hydrogen.

The steelmaking process for this steel grade includes smelting of liquid semiproduct in the electric arc furnace DSP-120, secondary refining process and ladle-vacuum treatment. The main technological task in melting of this semiproduct is obtaining of a final phosphorus content not more than 0.003% using deep dephosphorization process. For this purpose solid carburizers in the charge, such as pig iron and coke, are replaced by pulverized carbon-containing materials, blowing-in with oxygen or adding to slag during oxidizing period. In order to organize the process of deep desulfurization simultaneously with the removal of hydrogen, it is necessary to obtain the optimal slag composition in the required amount and high deoxidation of the metal before ladle vacuum treatment. Deep bulk deoxidation was carried out immediately during discharge of liquid semiproduct out of the electric arc furnace. Regulated content of the following elements was obtained as a result of usage of these methods: phosphorus 0.003–0.004%, sulfur 0.001–0.002%, hydrogen 0.8–1.1 ppm, oxygen activity 3–5 ppm.

I. Introduction

Rise of efficiency and safety of nuclear power engineering require increase of service life of nuclear power plants (NPP) and level of their reliability. It concerns to the shells of nuclear reactors (NR) in the most degree because just they determine the resource of nuclear power plants in general [1–3]. It also stands the new requirements to the materials for large shell products. NR shells are large and complexly loaded products and shell materials are subjected during operation to mechanical loading at high temperatures as well to thermal and radiation (for NR shell) embrittlement [4–10]. Resource of shells is determined by saving of the required level of tough–ductile properties, what requires rise of their initial level as well

* A. P. Kulikov, V. A. Tsarev, V. A. Novikov and D. S. Tolstykh participated in this research.

as decrease of their degradation rate during operation. These tasks can be solved both due to development of the new shell materials and to improvement of the complex of properties of the existing ones. In this case restriction of content of harmful elements and impurities (first of all — phosphorus, sulfur and hydrogen) is one of the most efficient methods for increase of shell service life based on the criteria of radiation and thermal embrittlement.

2. Problem setting

The manufacturing technology for 15X2HMФА (15Kh2NMFA) (А—А, class 1) steels used for nuclear reactors (see tab. 1) include melting of a liquid semifinished product in electric arc furnace DSP—120 and its finishing in the ladle refining and vacuum treatment units UVRV—1 and UVRV—3 (fig. 1 and fig. 2).

It was required to conduct the following investigations.
1. Manufacture of liquid semifinished product in the electric arc furnace to provide the required content of harmful impurities.
2. Development of the technology of finalizing of liquid steel during ladle treatment to provide the required parameters of liquid metal before casting, i.e. to provide the chemical composition.
3. Research of dephosphorization, desulphurization and degassing of 15X2HMФА (15Kh2NMFA) (А—А, class 1) steels used for nuclear reactors.

3. Description of investigation

Investigation of the technology aimed in improvement of metallurgical quality has been conducted in the conditions of “OMZ (United Machine—building Works) Spetsstal” enterprise, at the electric arc furnace DSP—120 and in the ladle refining and vacuum treatment. The main technological problem in melting of a liquid semifinished product is conducting of the process of deep dephosphorization and obtaining of final phosphorus content not more than 0.003%. Large number of works [11—14] has been devoted to investigation of this process, but the final phosphorus content in these researches made usually 0.010—0.015%. Thereby it was necessary to pay special attention in the investigations of melting technology of extra low—phosphorus steels to the parameters determining deepness of dephosphorization process, such as basicity, oxidation and amount of slag.

Considering the ladle treatment, it should be underlined that the company “Izhorskie zavody” (now “OMZ Spetsstal”) was a pioneer in mastering of ladle treatment technology on the equipment delivered by ASEA and SKF companies in 1980—ies. This technology was developed taking into account the existing equipment at that time.

4. Obtained results and their analysis

Modernization of the technology for liquid semifinished product melting in the electric arc furnace DSP—120 concerned both the composition of charge materials and directly the method of process implementation. Solid carburizers in charge material, such as iron and coke, were replaced by pulverized carbon—containing materials (such as UMVK, USM) that are blowing in the furnace together with oxygen or adding to slag during oxidizing period. The amount of carbon—containing materials is in the range 5—20 kg/t, their feed rate makes 20—30 kg/min and oxygen consumption varies up to 30 m³ (see tab. 2, a).

Dosed injection of pulverized materials on the boundary of “metal — slag” separation provides optimal oxidation and basicity of slag. Slag basicity for CaO/SiO₂ compound makes ~ 4—5 units, while oxidation is equal to 16—23% (see tab. 2, b). It should be underlined for comparison that excessive slag oxidation (up to 50% FeO)

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
<th>Cu</th>
<th>S</th>
<th>P</th>
<th>As</th>
<th>Co</th>
<th>Sn</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>15Kh2NMFA</td>
<td>0.13—0.18</td>
<td>0.17—0.25</td>
<td>0.3—0.6</td>
<td>1.8—2.3</td>
<td>1.0—1.5</td>
<td>0.5—0.7</td>
<td>0.10—0.12</td>
<td>≤ 0.3</td>
<td>≤ 0.008</td>
<td>≤ 0.008</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15Kh2NMFA—A</td>
<td>≤ 0.1</td>
<td>≤ 0.007</td>
<td>≤ 0.007</td>
<td>≤ 0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15Kh2NMFA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>≤ 0.06</td>
<td>≤ 0.005</td>
<td>≤ 0.006</td>
<td>0.01</td>
<td>≤ 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>class 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
in the former, classic technology often has led to low slag basicity (less than 2.5 units).

Refuse of iron use in charge material allowed to decrease initial phosphorus content by 0.01%. Relatively low initial phosphorus content in charge material (~0.01–0.015%) and optimal slag composition made it possible to obtain phosphorus content just during melting at the level not more than 0.005–0.007% and to decrease it before tapping down to 0.003% (see tab. 2, a).

It should be mentioned that injection of large amount of carbon materials with sulfur content up to 0.8% leads to increase of sulfur concentration in a liquid semiproduct up to 0.020–0.038% (in addition to the positive effect).

Inauguration of oxidation control before tapping is considered as the important improvement of the melting technology for a liquid semiproduct in the electric arc furnace DSP—120. Measurements of oxygen activity in the melt allow to provide express analysis for de-

### Table 2. Charge material, variations of metal (a) and slag (b) chemical composition in the electric arc furnace DSP–120

<table>
<thead>
<tr>
<th>No. of melt</th>
<th>Charge material, t</th>
<th>Fluxes, t</th>
<th>Chemical composition, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HBI PCB(^1) Wastes Al(_2)O(_3) MgO SiO(_2) P(_2)O(_5) S CaO TiO(_2) Cr(_2)O(_3) MnO FeO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>124446</td>
<td>89 43.8 16.0 0.207 — 4.0 3.0 2.0 1.5 1.0 1.0</td>
<td>C P S (\nu_0)</td>
<td>0.11 0.005 0.038 0.0795</td>
</tr>
<tr>
<td>1497007</td>
<td>Yield 115.0 t Heel 14.0 t</td>
<td>0.035 0.003 0.027 60°</td>
<td></td>
</tr>
<tr>
<td>124447</td>
<td>89.5 43.2 16.0 Болото –14.0 0.206 — 2.0 3.0 2.0 1.0</td>
<td>0.09 0.04 0.027 0.0393</td>
<td></td>
</tr>
<tr>
<td>163005</td>
<td>Yield 115.0 t Heel 10.0 t</td>
<td>0.07 0.003 0.03 0.039</td>
<td></td>
</tr>
<tr>
<td>124448</td>
<td>Болото –10.0</td>
<td>0.05 0.003 0.022 0.025</td>
<td></td>
</tr>
<tr>
<td>113.0 t</td>
<td></td>
<td>0.07 0.003 0.022 0.025</td>
<td></td>
</tr>
<tr>
<td>1244488</td>
<td>73.6 0.115 — 4.0 3.0 1.5 5.0</td>
<td>0.11 0.007 0.022 0.0375</td>
<td></td>
</tr>
<tr>
<td>89875</td>
<td>8.2 t Heel</td>
<td>0.05 0.003 0.022 0.0375</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) Passport Charge Billet;
*— numerator: for melting; denominator: before tapping.

### Fig. 3. Variation of hydrogen and sulfur content in the metal during ladle treatment with two (a) and one (b) vacuum periods
termination of carbon content and timely termination of oxidizing period without excessive over-oxidation of metal and slag and increased metal waste. In this case, when carbon content is restricted by 0.08–0.1%, oxygen activity was in the range 250–600 ppm (see table 2, a).

When we consider the process of ladle treatment, it should be reminded again that the company “Izhorskie zavody” (now “OMZ Spetsstal”) was a pioneer in mastering of ladle treatment technology on the equipment delivered by ASEA and SKF companies in 1980–ies based on the production facilities operated at that time. The process with double vacuum treatment has been developed and mastered for extra high-duty products (see fig. 3, a). The first vacuum period was used mainly for solving the problem of hydrogen removal and vacuum carbon deoxidation of metal and slag. Usage of this scheme was caused by the absence of reliable systems for bottom argon blowing of metal during the period of development of this technology. Thereby it was necessary to organize vacuum carbon “boiling” and hydrogen removal into floating carbon oxide bubbles to realize dehydration. It was shown (see fig. 4, a), that oxidation of ~0.02% of carbon during vacuum treatment is required for efficient hydrogen removal [15].

Appearance of the new argon blocks provided practically 100% guarantee of reliability of the blowing process. The conducted calculations displayed that argon consumption should make 3.0–4.0 m³ at [H₀] = 3.0–4.0 ppm and Pₜ₉₀ = 1 mm Hg for efficient hydrogen removal from deoxidized metal in 100 t ladle down to 1.0 ppm (see fig. 4, b).

Multiple experimental data obtained during treatment of different steel grades have confirmed these results (see fig. 5). It can be seen that hydrogen content during vacuum treatment of deoxidized metal decrease (depending on the season) from 2.5–4.0 to 1.1–1.5 ppm. It was a prerequisite to transition to the ladle treatment route with one vacuum period, including steels for nuclear power stations (see fig. 3, b).

To organize the process of deep desulfurization together with hydrogen removal, it is necessary to provide the optimal slag composition in the required amount as well as high degree of metal deoxidation before vacuum treatment [16–19]. Previously developed technology envisaged step-by-step conducting of these processes with preliminary vacuum carbon and consequent deposited and diffusion deoxidation [20].

In the modernized variant, deep deposited deoxidation is conducted just during tapping of liquid semiproduct out of the arc furnace (see fig. 3, b). Added amount of bulked and pulverized aluminium makes 2.0 kg/t (0.2%) and 1–3 kg/t. This amount should be sufficient not only for metal and slag deoxidation, but also for melt protection from secondary oxidation during tapping. As a result, it is possible to have completely deoxidized metal and slag already in the beginning of the treatment.
Ladle treatment of the first four melts of 15Kh2NMFA (class 1) steels via the new technology was finalized in the following results. Aluminium content in the metal before vacuum treatment made 0.01–0.05% and content of Fe, Mn, Cr oxides in slag didn’t exceed 0.3% for each of them. Slag basicity was in the range 4–12.

Solving the problem of dehydrogenization was not connected with any doubts, taking into account the accumulated experience. Metal blowing in vacuum conditions with argon (consumption 4.2–5.6 m³) provided its final content in the range 0.9–1.4 ppm.

It was more difficult to solve the problem of deep desulfurization, taking into account increased sulfur content (0.030–0.022%) and aim to obtain the final sulfur concentration not more than 0.002%.

In accordance with the developed technology of slag deoxidation and forming the liquid slag layer on metal surface, sulfur content in metal during ladle—to—ladle tapping and reheating decreased from 0.016–0.030% to 0.004–0.007%. At the same time its concentration in slag increased to 0.35–0.60%. The actual coefficient of sulfur distribution between metal and slag made 50–75 units. Its equilibrial values for the obtained and practically ideal slag composition achieve 300–1500 units (see fig. 6, a). It seems that large reserve of sulfide capacity can be easily realized in the following powerful metal stirring during vacuum treatment with argon blowing. But practical experiments displayed that the average value of maximal actual values of the distribution coefficient after vacuum treatment made about 300 units.

Slag amount makes usually ~ 2.5% of metal weight. Taking into account this information, we can conclude that final sulfur concentration depends mainly on its initial content in metal and slag. Initial slag content in metal is a preset value. Thereby it is a real option to influence during ladle treatment on final sulfur content in metal via lowering of its content in slag by its renovation. The required maximal allowable sulfur content providing the aimed final sulfur concentration in metal is shown on the fig. 6, b. It can be seen that initial sulfur concentration in metal and slag should not be more than 0.0015% and 0.08% respectively, to provide the final sulfur content in metal equals to 0.002%. The mentioned sulfur content in slag corresponds to sulfur content in lime — the main slag—forming component.

To provide the final sulfur concentration 0.001%, the initial sulfur content in metal should be not more than 0.006% or 0.002%, when the initial sulfur content in slag is 0.08% or 0.26% respectively. And to achieve the final sulfur concentration in metal 0.0005%, the initial sulfur content in metal should be not more than 0.0002% and its initial content in slag should not exceed 0.08%.

Taking into account the high initial sulfur content in metal (more than 0.015%), we can testify that partial or complete slag renovation is required in this case to achieve sulfur concentration 0.002%.

The first melts conducted with slag renovation have confirmed completely all calculated data. Slag renovation allowed to decrease its initial sulfur content from 0.6% to 0.35–0.18%. The process of deep desulfurization was successfully conducted due to consequent intensive metal and slag stirring in vacuum conditions.

Sulfur content 0.001% has been obtained for the first time for two melts, and sulfur content 0.002% – for two other melts (see tab. 3, a). Oxygen activity in metal before tapping made 3–6 ppm for aluminium content 0.007–0.015%.

The ingot with mass 335 t has been manufactured from three melts of 15Kh2NMFA (class 1) steel (see tab. 3, a). Tapping has been conducted in vacuum conditions using a tundish. The billet of elongated rim of the active part of VVER—1000 reactor shell for the Belarus nuclear power station has been manufactured from this ingot. Expertise of the billet metallurgical quality has shown that its microstructure meets the requirements of the technical conditions and such unallowable defects as cracks, flakes, laminations, shrinkage porosity were not revealed. The results of final control of contamination of the billet feeder part with non—metallic inclusions also confirmed correspondence with the requirements of technical regulations (see tab. 3, b).
5. Conclusions

The developed and tested new melting technology allows to meet completely up-to-date strict requirements for metal quality with perspective of their future elevation. It is possible to regulate phosphorus content at the level 0.003–0.004%, sulfur content — 0.001–0.002%, hydrogen content — 0.8–1.1 ppm and oxygen activity — 3–5 ppm. The developed technology provides manufacture of steel with extra cleanliness for harmful elements and makes it possible to improve substantially the complex of properties of prospective shell materials, what will lead to rise of efficiency and safety of the nuclear power industry.


REFERENCES

17. Dub V. S. To research, develop and put onto practice the technology of deep desulfurization and dephosphorization of structural steels applying to the conditions of “Izhorsky zavod”. TsNIITMASH Report. 1985. 42 p.

Table 3. Final content of harmful impurities, hydrogen, oxygen and aluminium in 15Kh2NMFA (A–A, class 1) steel, % (a) and the results of final control of contamination of the billet of nuclear reactor shell rim from the 335 t ingot (b)

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>No. of melt</th>
<th>P, %</th>
<th>S, %</th>
<th>H, ppm</th>
<th>Pp, ppm</th>
<th>Al, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>15Kh2NMFA–A class 1</td>
<td>188437</td>
<td>0.003</td>
<td>0.001</td>
<td>1.4</td>
<td>5.0</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>197865</td>
<td>0.004</td>
<td>0.002</td>
<td>1.1</td>
<td>3.0</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td>100806</td>
<td>0.006</td>
<td>0.002</td>
<td>0.9</td>
<td>4.0</td>
<td>0.007</td>
</tr>
</tbody>
</table>

(a)

<table>
<thead>
<tr>
<th>Sulfides</th>
<th>Spot oxides</th>
<th>Linear oxides</th>
<th>Brittle silicates</th>
<th>Ductile silicates</th>
<th>Non-deformed silicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
</tr>
</tbody>
</table>

(b)

Final values (feeder part) 0.0 1.0 0.0 1.3 0.0 1.2
Requirements of technical regulations TU 0893–013–2003

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