CHALLENGING TECHNOLOGIES OF MANUFACTURE OF HIGHLY-RELIABLE PRODUCTS OF STRUCTURAL STEELS FOR BASIC BRANCHES OF INDUSTRY

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The main elements of new complex technologies providing the efficient production of materials with a new level of properties were considered. The prospect of development of new systems of alloying of structural materials for machine building with control of their primary crystalline structure, mechanisms of strengthening, resistance to brittle fractures was noted. 4 Tables, 10 Figures.

Keywords: *technological and materials science principles, complex technologies, structural steels, basic branches of industry, challenging research directions*

New requirements to reliability require application of new technological and materials science principles. The relation of «micro-meso-macro» parameters of structure of materials (Table 1), introduced during transition from liquid state into solid one, i.e. from the very beginning of technological route, requires application of new scientific and technological approaches to the development of new technologies. The old technologies allowed removing only rough discrepancies between the requirements and a real quality.

The industry branches which require development of new technologies and materials:

Table 1. Levels of structure

Microlevel ($\leq L_0$)	
Vacancy, atom	$2–3\cdot10^{-10}$ m
Clusters	$2–5\cdot10^{-9}$ m
Dislocation	10^{-8} m
Meso-level	
Block of mosaics, subgrain, sulphides, NI	$10^{-7}–10^{-6}$ m
Level of grain L_s	
Grain, dendrite, sulphides, NI	$10^{-5}–10^{-4}$ m
Macrolevel ($>L_s$)	
Group of grains	$2–5\cdot10^{-4}$ m
Specimen area	10^{-3} m
Specimen as a whole	More than $10^{-3}–10^{-2}$ m

Power engineering, heat power complexes, nuclear power engineering: pipelines, wind power generators, stop valves; heat resistant scarcely-alloyed materials for supercritical parameters (SCP) of work; blades for the stages of gas turbine plants (GTP); structural materials with improved working characteristics for reactor units, turbines with service life of more than 60 years;

Chemical industry: structural materials for reactors and high-pressure pipes;

Transport and main gas pipelines: new materials for railroads, ship building, pipes of high strength;

Products of defense industry.

The important stage in formation, investigation and control of properties of metal products is solidification process. It is composed of a number of physical and physical-chemical processes, where solidification stage is a key one, i.e. the phase transition itself of the first kind: liquid (melt)-solid body (crystals).

As far as all the real metallic systems, used for manufacture of products, are multicomponent, it is very important to understand the level of agitation which is introduced into regularity of crystalline structure of alloy base (iron, as in our case) by each participant of the composition. In the first turn it is rational to distinguish most strongly agitating elements. For such evaluation the most suitable is the expression, which Chalmers called the accommodation coefficient A_c:

$$A_c = e^{-\frac{\Delta H_s}{RT_m}}, \quad (1)$$

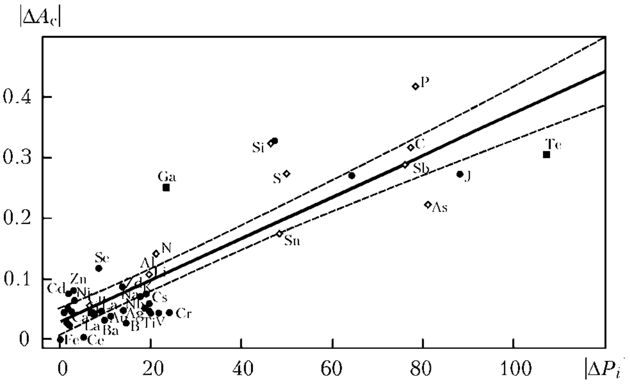

Figure 1. Relation of potential of ionization ΔP_i and ΔA_c

where A_c is the accommodation coefficient; ΔH_s is the latent heat of solidification; T_m is the solidification temperature.

In case of melting Ac is accepted equal to 1.

For quantitative measure of agitation evaluation caused by impurity during solidification, the expression was derived (2):

$$|\Delta A_c| = A_c^{Fe} - A_c^{B}. \quad (2)$$

As a result of calculation $|\Delta A_c|$ the elements having the strongest agitating influence on solidification of iron-based alloys were arranged in a row according to the level of their decrease:

P, Si, C, S, Sb, As, Bi, Sn, N, Cu, Al, Mn. (3)

The value $|\Delta A_c|$ has a good correlation with the potential of ionization ΔP_i integrally describing the thermophysical peculiarities of a single element (Figure 1).

Based on the hypothesis of two-stage mechanism of solidification process (atomic melt–cluster-atomic boundary layer — joining of clusters to crystalline front), the crystallization and influence of thermophysical (solidification rate) and physical-chemical (concentration and $|\Delta A_c|$ impurities) factors on the fractal dimension D as the characteristics of regularity of the crystalline matrix structure (Figure 2) were modeled. As is seen from the succession (3), silicon has a very strong influence on the solidification process of iron-based alloys. Figure 3 shows the results of experimental and calculation study of effect of silicon and ΔA_c on the structure of structural Cr–Ni–Mo steel.

During crystallization of steel, phosphorus has also the equally strong influence. In connection with the fact that influence of agitating elements is added, their effect is either intensified or in case of presence in the amount of less than critical concentration, it is weakened (Figure 4).

Simultaneously with the processes violating the regularity of constitution of crystalline structure, the phenomena are developed facilitating the decrease of resistance to degrading loads (thermal, atomic, periodically force, etc.). The data of Table 2 prove the relation between violation of regularity of constitution at the presence of definite impurity $|\Delta A_c|$ and tendency of material to embrittlement.

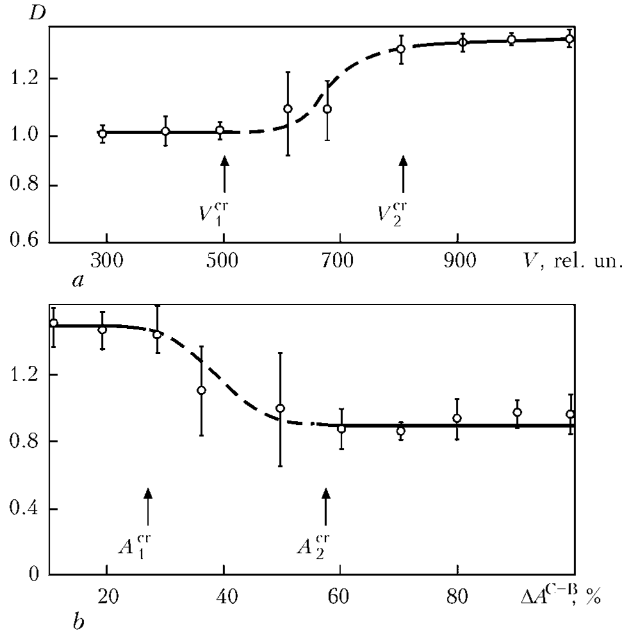

Figure 2. Dependence of fractal sizes D of model structures on the cooling rate V (a) and relative accommodation coefficient ΔA_c (b)

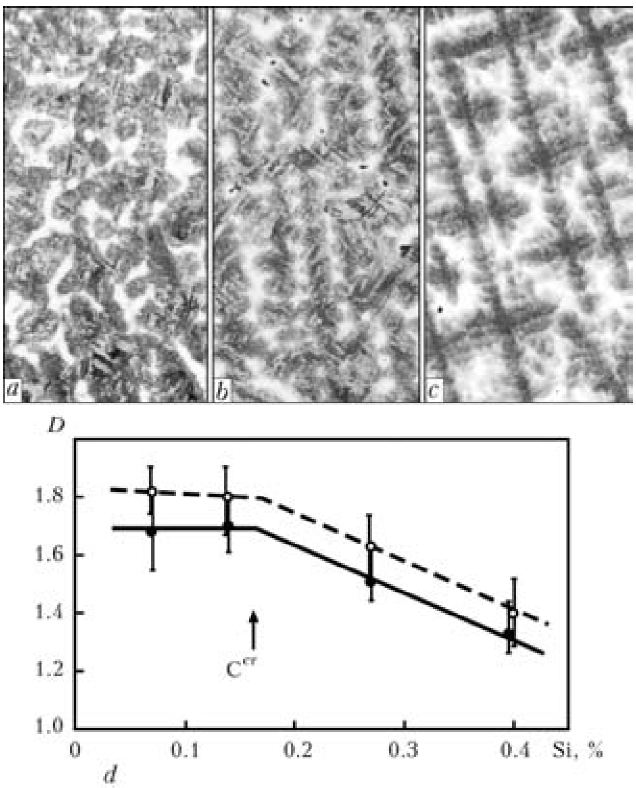

Figure 3. Microstructure of specimens at different content of silicon (a–c): a — 0.05 %; b — 0.15; c — 0.27; d — dependence of fractal sizes D of model structures on silicon content

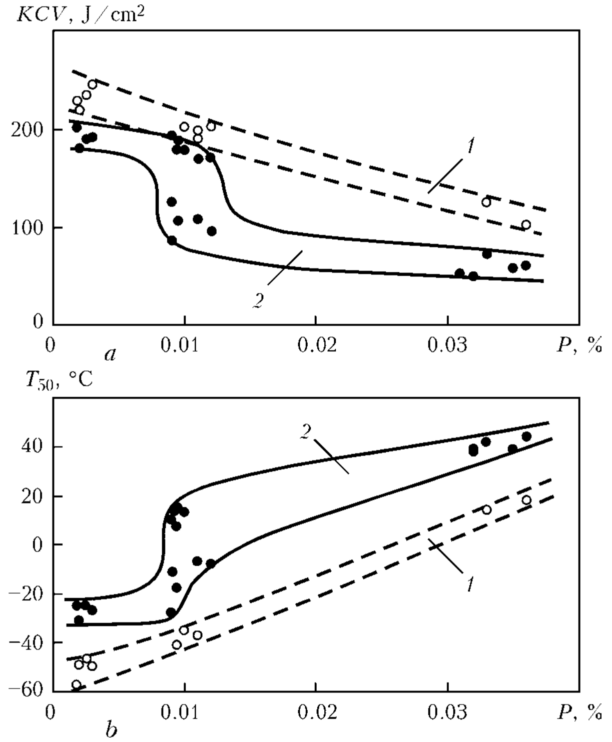

Figure 4. Influence of phosphorus and silicon on the change of impact toughness (*a*) and temperature of brittle-tough transition (*b*): *1* — <0.1 % Si; *2* — ≥0.1 % Si

The modern concepts about the nature of embrittlement of steels are based on formation of preliminary segregation (precipitates) and segregations (phosphorus, sulfur, tin, antimony and other elements) and intensifying action of alloying elements, such as silicon, nickel, manganese, the influence of which strongly depends on their concentration.

The important problem in this case is the state and extension of grain boundaries. The greatest attention was always paid to the investigation of the state of grain boundaries in the metal of body equipment of the nuclear power plants (NPP). In the last period in connection with the requirements to increase the life and reliability of these products and also to provide the competitive advantages of domestic nuclear power equipment in the OJSC SPA «CNIITMASH» the works are systematically carried out on study of mechanisms of formation of grain boundaries, evaluation of their influence on properties of products and development of technological methods of control of quality and properties of boundaries.

Using the gained experimental material, the procedure of modeling was developed to evaluate the sizes of grains of primary crystalline structure and their evolution at different operations of deformation. The work like this and in such a volume is carried out in our country for the first time.

The evaluation of elements with the strongest influence on the state of boundaries was carried out. As the example, the behavior of phosphorus, the element considerably influencing the state of boundaries at all the stages of technological route and during service, was studied. As is known, phosphorus is the element the accommodation coefficient of which is strongly differed from that of iron. Therefore it is a strongly liquating element, the equilibrium distribution coefficient of which is very low during crystallization (K_0 is less than 0.1). Due to this, during solidification of large ingots used in production of body equipment of the nuclear power plants, this element is non-uniformly distributed accumulating itself in the interdendrite spaces (microliquation) and in the zones of chemical heterogeneity (sub-crop zone and in the zone of out-of-centre liquation). The thermodynamic approaches are known, which allow observing the changes in phosphorus concentration. The calculated values show the concentration level of impurity which can be expected at boundaries in the product made of a relatively large ingot with the average radius of more than 400 mm.

It should be noted also that as far as K_0 is the thermodynamic characteristic, it was assumed that it does not depend or scarcely depends on the concentration of liquating element. However in the recent works, including the works of associates from the OJSC SPA «CNIITMASH», it was shown, that in case of impurity concentration in the melt approximating to the solubility limit of this element in solid iron, the values K_0 grow abruptly.

Considering these approaches and experimental results on study of dendritic structure of cast steel 15Kh2NMF, the concentration of phosphorus in the boundary layer was calculated which is the pre-image of boundaries in the future product (proto-boundary), and at the final stage it

Table 2. Dependence between $|\Delta A_c|$ and embrittlement of low-alloyed steels

Parameter	Fe	Cu	N	C	Si	P
A_c	0.360	0.303	0.503	0.042	0.037	0.778
$\lvert\Delta A_c\rvert = \lvert\Delta A_c^B\rvert - \lvert\Delta A_c^{Fe}\rvert$	0	0.057	0.143	0.318	0.323	0.418

is the level of filling the boundary layer with phosphorus atoms depending on the grain size.

The investigations showed that the degree of filling the sites, suitable for absorption, with phosphorus by 0.1 results in increase of critical temperature of brittleness by 27–28 °C. As a result it was succeeded to obtain dependence of effect of phosphorus content in metal before solidification and grain size of a ready product on the increase of critical temperature of brittleness. The results of ΔT_{k0} changes are presented in Figure 5. It is important that manufacture of ready-metal products of steel 15Kh2NMF the grain size which is higher than the definite one (more than 6–8 marks) provides high stability against brittle fractures, and decrease of phosphorus content in initial metal to less than 0.004 % makes steel almost insensitive to the degrading effects.

The progress in manufacture of highly-reliable products, for example, of bodies of nuclear and oil chemical reactors, welded rotors, etc. is connected also with the further promotion of decrease in T_{k0} of weld metal. The OJSC SPA «CNIIT-MASH» developed the program of technological and organization measures, including, for example, modernization of production of fused fluxes.

It is known that the weld metal has a number of peculiarities as compared to the base metal, as far as it is serviced in a cast state. The embrittlement of Cr–Ni–Mo welds (Ni << 1.5 %, P << << 0.012 %) at delayed cooling during tempering is predetermined by the content of silicon, manganese and nitrogen above the definite level (Figure 6). The technological measures of solution of task as-applied to the body of WWER-1000 are mostly known and achievable at present:

• Restriction of nitrogen content is achieved by degassing in melting steel for welding wire;

• Restriction of silicon and manganese content in steel for wire;

• Control of transition of silicon and manganese in the process of welding into the zone «slag-welding pool» by regulation of electric parameters of welding mode;

• Purposeful creation of combination «melting of wire-flux batch» (instead of selective application of accidental flux batches).

To realize the scientific developments is only possible by the use of new technological processes or by system application of formerly prepared technological solutions, combining them in the strictly determined standard consequence and alternating them with the newly recommended procedures:

The basic elements of new technologies:

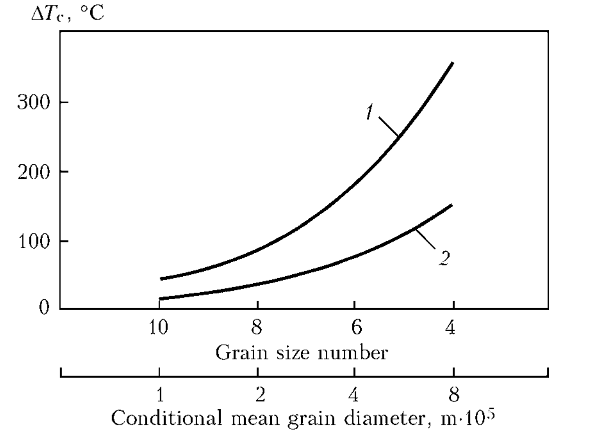

Figure 5. Influence of phosphorus content in metal before solidification and grain size of ready-made product on the increase of critical temperature of brittleness: *1* — initial concentration of phosphorus in liquid metal 0.01 %; *2* — 0.003

Steel melting cycle:

• Modern equipment for charge preparation, the modern charge materials strictly controlled as to their composition, type and sizes;

• Modern steel melting equipment providing efficient melting, strictly controlled oxidized processes (decarburizing, deep dephosphorizing) or absence of oxidation (complete remelting);

• Modern equipment for ladle treatment of liquid semi-product providing degassing, intensive fulfillment of reduction reactions (deep desulphuration, deoxidation, control of oxidation and control of oxide morphologies), precise alloying, strictly controlled heating and intensive stirring.

Cycles of solidification and pouring:

• Application of specialized fixture, which provides its optimal heat work and rational use of cast billet (shape of ingot corresponding to the product purpose);

• Application of rational method of casting (from the top, siphon, in vacuum or specialized atmosphere);

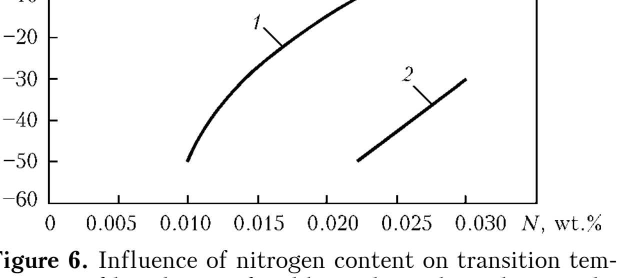

Figure 6. Influence of nitrogen content on transition temperature of brittleness of weld metal T_{k0} depending on the total concentration of silicon and manganese 0.7 % (*1*) and 0.6 (*2*)

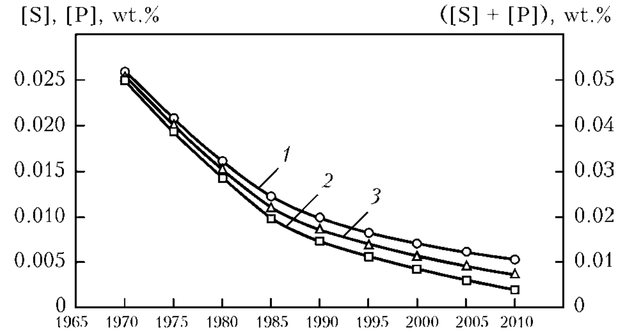

Figure 7. Dynamics of changes of admissible content of impurities in the steels for power machine building: *1* — [P]; *2* — [S]; *3* — [P] + [S]

• Standard state of liquid metal before pouring (strictly regulated chemical compound, oxidation, hydrogen content, temperature);

• Protection against contact with environment (protection against secondary oxidation, saturation with hydrogen and nitrogen);

• Differentiated and controllable temperature-speed mode of pouring.

Deformation processing:

• Modern furnace, forge-press equipment, providing necessary distribution of temperatures before deformation accounting for accumulated deformation and its speed;

• Modern fixture, measuring electron tool;

• Program deformation considering the data about quality and peculiarities of initial billet (ingot, ESR ingot, forged billet).

Heat treatment:

• Differentiated modes considering the results of evaluation of characteristics of an ingot (chemical composition, hydrogen content, amount of inclusions) and deformed billet (maximum grain size, distribution of non-metallic inclusions and zones of chemical heterogeneity);

• Modern thermal furnaces with admissible non-uniformity of thermal field in the range of up to 5 °C, the application of vertical furnaces with the bottom installation device;

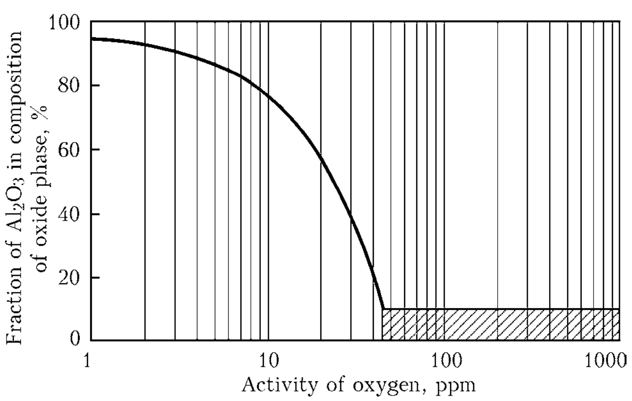

Figure 8. Influence of activity of oxygen on content of Al_2O_3 in the composition of non-metallic phase (for steel with 9 % Cr)

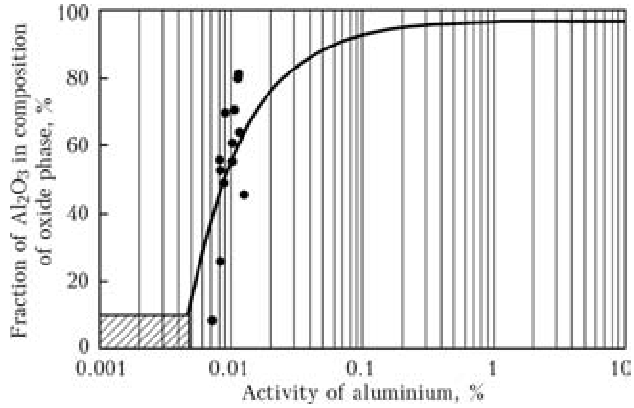

Figure 9. Influence of activity of aluminum (concentration) on the content of Al_2O_3 in the oxide inclusions of steel 15Kh2NMFA (curve was obtained under the laboratory conditions)

• Modern thermal spraying units (mostly of vertical type), modern quenching devices and media.

Welding and mechanical treatment stage:

• Modern means of control and metrological equipment;

• Welding consumables adapted to the base metal;

• Welding fluxes, providing both protection as well as formation of preset properties and quality of weld material;

• Increase of share of automated processes, application of three-coordinates welded and surfaced heads;

• Application of modern processes of finishing treatment not resulting in accumulation of stresses in the product.

Let us study some examples of application of modern technologies.

Figure 7 shows dynamics of changes in the admissible content of controllable impurities in the materials used in the nuclear and convection power engineering and other important areas of economy. The results show that for today the technology allows approaching the limit of solubility of sulfur and phosphorus in the steels and, thus, finding a radical solution of the problem

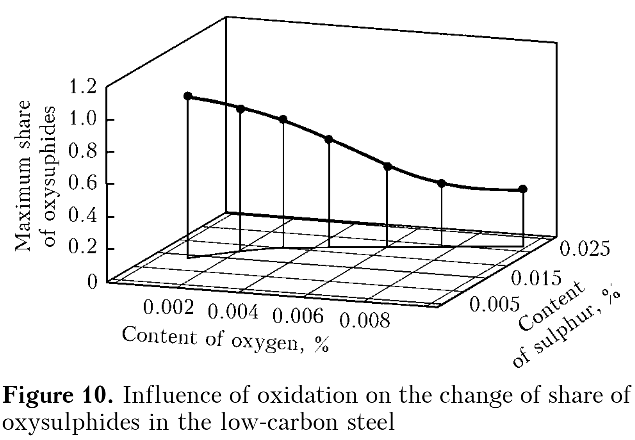

Figure 10. Influence of oxidation on the change of share of oxysulphides in the low-carbon steel

Table 3. Characteristics of the steels 15Kh2NMFA-A, 15Kh2NMFA-F of class 1

Part	Volume of sampling	Mechanical properties, +20 °C			
		σ_t, MPa	$\sigma_{0.2}$, MPa	δ, %	ψ, %
TS 0893-013-00212179–2003 (with changes No. 2–2011)		610	490	15	55
Shells of active zone (support, upper and lower)	48	712	607	21.8	75.6
Flanges of lid and body	44	700	602	20.0	74.0
Shells of zone of pipe branches	45	691	582	21.0	75.0
Bottom of body, ellipsoid of a lid	66	715	602	20.0	73.0
Shell of zone of pipe branches for the Baltic NPS	First	670	565	24	76.0

Table 3 (cont.)

Part	Volume of sampling	Mechanical properties, +350 °C				T_{k0}	Notes
		σ_t, MPa	$\sigma_{0.2}$, MPa	δ, %	ψ, %		
TS 0893-013-00212179–2003 (with changes No. 2–2011)		539	441	14	50	–45 °C — for shells of active zone, –35 °C — for shells of the pipe branch zone, –20 °C — for bottom and ellipsoid, flanges of lid and body	The set values of T_{k0} are based on the real experience of manufacture of KR WWER-1000
Shells of active zone (support, upper and lower)	48	595	518	17.0	74.0	–50 – –75	For reference: 37 units WWER-1000 and WWER-1200
Flanges of lid and body	44	585	517	15.0	75.0	–50 – –80	
Shells of zone of pipe branches	45	572	495	16.0	73.0	–50 – –75	
Bottom of body, ellipsoid of a lid	66	592	517	15.0	70.0	≤–70	
Shell of zone of pipe branches for the Baltic NPS	First	547	472	16.5	72	–90	Mastering of production at PJSC «EMSS»

Note. During the whole time of production none of the shells for reactor body had any inadmissible deviations from the requirements of TS.

of chemical heterogeneity and embrittlement of structure materials connected with it.

The control of the composition and morphology inclusions in different materials for power engineering are given in Figures 8–10.

The application of number of technological solutions mentioned above allowed the improvement of technology of production of equipment for the nuclear power station to the higher level which turned to be a principally new stage in development of metallurgy both for the nuclear machine building as well as machine building in general. The increased requirements to the cleanness of metal, intensive refining, new technology of pouring, forging and heat treatment, accepted for bodies of reactors of the project NPS-2006, allowed obtaining the very low real values of critical temperature of brittleness in manufacture for all the elements of body and lid of reactor (below 90 °C) (Table 3).

Table 4. Chemical composition of steel for collectors of steam generators of the type PGV-1000MKP, wt.%

Grade of steel	C	Si	Mn	Ni	Mo	W	Cr	Cu	S	P
							Not more than			
10GN2MFA-VD 10GN2MFA-Sh	0.08–0.12	0.17–0.37	0.80–1.10	1.8– 2.3	0.40–0.70	0.03–0.07	0.30	0.30	0.005	0.008
10GN2MFA-A	0.09–0.11	0.20–0.30	0.90–1.00	1.8–2.0	0.55–0.65	0.04–0.06	0.15	0.15	0.002	0.006

Note. In steel 10GN2MFA-A the content of Sn, As, Sb and Kh = (10P + 5Sb + 4Sn + As)·100 ≤15 is determined.

One more example of application of new approach to the technology is the development of especially pure modifications of steel grade 10GN2MFA-A, in which the contents of sulfur and phosphorus are considerably decreased, the limits of content of basic alloyed elements are narrowed, the determination of content of arsenic, tin and antimony with regulation of X-factor (X = (10P + 5Sb + 4Sn + As)·100) (Table 4) was introduced.

It also should be noted that at the present time in the OJSC SPA «CNIITMASH» to decrease the critical temperature of brittleness and stabilization of properties in welding the investigations on determination of mechanism of effect of complex modifiers, added to the weld metal through the ceramic flux, on mechanical characteristics of weld metal are carried out.

The tests of mechanical properties of metal of welds produced in welding of pilot specimens of steel 15Kh2NMFA using pilot compositions of ceramic fluxes FTsK-16 in combination with the wire SV-12Kh2N2MAA evidence of high level of mechanical characteristics of weld metal, increasing the requirements of standard documentation. The tests in welding under the flux KV-4 showed that the critical temperature of brtittleness amounts to $T_{k0} = -30$ °C.

Conclusions

At the present time there are elements of new complex technologies which were tested and implemented providing effective manufacture of materials with the new level of properties.

The further searches in the area of complex technological and materials science investigations are directed to the creation of new systems of alloying of structural materials for machine building, oriented to the control of the primary crystalline structure, by the strengthening mechanisms, mechanisms of resistance of metals to brittle fractures.

It is necessary to develop new systems of technological and standard documentation relying also on the use of objective in-process methods and creating conditions for continuous electron monitoring of technology allowing its correction according to the in-process values obtained at the previous stage.

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