

DEPENDENCE OF THE NITROGEN SOLUBILITY IN AUSTENITE AND FERRITE ON ALLOYING AT THE ELEMENTAL LEVEL.

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SUMMARY: There are adduced classical functions of the nitrogen solubility in ferrite and austenite caused by alloying at the intratomic level there. For its calculation the empiric thermodynamic model, reflecting the accumulated elemental influences by the example of iron, chrome, manganese, nickel through the whole solid metal temperature range was suggested, which enables the determination of maximum metal alloying level, ensuring the non-defect structure by crystallization. The model was built according to the Hume-Rothery's principle on the grounds of common functional thermodynamic descriptions of alloying elements and iron electronic configurations, being uniform for austenite and ferrite, as well as dependence of size factor for each component on these configurations.

Analysis of coefficients in the proposed ferrite and austenite solubility model enables the evaluation of difference of the nitrogen introduction structural nature for these metals by alloying with considered elements.

KEY WORDS: Nitrogen, solubility, ferrite, austenite, electronic configuration.

1. Introduction.

The nitrogen solubility in the high-chromium steels, as also in iron, for practical purposes described by thermodynamic methods by Taylor series expansion of coefficients of alloying elements [1,2] influence. Given approach allows description of solubility with the sufficient accuracy within the concentration and temperature range being studied, but it is limited with application of determined rules out of limits of the being analyzed and rather narrow temperature interval, e.g. near the crystallization temperature.

2. The Model of nitrogen solubility in high-chromium ferrite and austenite

According to the previously published classical regularity on the intratomic level, there was suggested to understand the t_{2g} -quantity of electrons [3] as the dependence (1) under the parameter $a(T)$ there.

$$\ln(a(T)) = \frac{A}{t + 273} + B; \quad (1)$$

where for iron $A = -1909$; $B = 2,528$.

Let's take the linear suborbital size t_{2g} as the atomics radius and designate e_g with the coefficient $r(P)$. Then the d-orbital size will be equal to:

$$R_r^r = \frac{[a_{\max}^j - a(T)]}{a_{\max}^j} \cdot r + \frac{a(T)}{a_{\max}^j} \quad (2)$$

where a_{\max}^j – quantity of electrons on the d-orbital of the j-element; T and T_c – current temperature and temperature of comparison $0,5^\circ\text{K}$.

Proceeding from the known distortion of the electronic suborbital e_g arrangement in the disintegration ($109,5^\circ$ angle instead of 90°), supposed being caused by the p^6 -shell [6] influence and under condition of permanent dimension of the electronic orbital e_g projection in the plane

(1;1;0) towards [11] over the p^6 -shell, its size in the distorted volumetric direction was found as:

$$r(P) = \frac{0,6}{\cos\left(\frac{109,5-90}{2}\right)\sqrt{2\cdot P}} \quad (3).$$

where P – pressure, atm; 0,6 — size of the electronic orbital e_g projection in the plane (1;1;0) towards [11] in atom size fractions.

Let's suppose the introduction of nitrogen and hydrogen atoms into the lattice as practicable owing to distortion of the suborbital e_g . Then, firstly, we will take the increment of fracture of all electronic orbitals at the temperature T in comparison with the temperature T_c , taken as $0,5^\circ K$, as proportional to the cube of the increment of linear dimensions amount of e_g - and t_{2g} -suborbitals:

$$\Delta Vel. orb.(j)_T^{r(P)} = \left(\frac{R_T^r}{R_{0,5^\circ K}^r}\right)^3 \quad (4)$$

Second, let's suppose the volume of pores, into which the nitrogen introduces, as proportional to the change of electronic orbitals volume with the distortion of e_g -orbital over the p^6 -shell in comparison with the volume without distortion, taking into account changes from $0.5^\circ K$:

$$V_{PIN,(j)T}^{\frac{0,6}{r}} = \frac{\Delta Vel. orb.(j)_T^{0,6}}{\Delta Vel. orb.(j)_T^r} - 1 \quad (5)$$

But the pores volume dimensionality is evaluated in atomic fractures of iron.

The electronic configuration parameter for the manganese in the solid state $a(T)$ was found proceeding from the temperatures of its allotropic transformations, proportional to expressions of whole numbers (Tables 1 and 2). The correlating factor value and graphical mapping of the obtained equation (Fig. 1) testify to the functional but not the static character of dependence.

As at the steels crystallizing temperatures the pure manganese is in the liquid state, its electronic configuration above its melting point was found in comparison with other elements: iron, silicon,

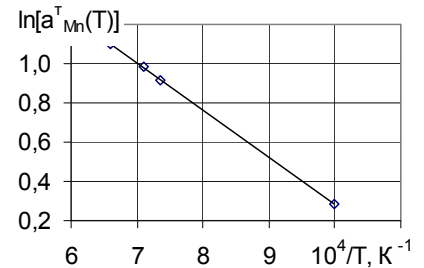


Fig. 1. Dependence of the electronic parameter configuration of manganese in solid state on temperature.

Table 1. Correspondence of the manganese electronic configuration parameter in solid state to temperatures of allotropic changes

Allotropic change	t, °C	$10^4/T, K^{-1}$	$a_{Mn}^s(T)$	$\ln[a_{Mn}^s(T)]$
$\alpha - \beta$	727	10,00	$1\frac{1}{3}$	0,288
$\beta - \gamma$	1087	7,35	$2\frac{1}{2}$	0,916
$\gamma - \delta$	1137	7,09	$2\frac{2}{3}$	0,981
$\delta - liquid$	1245	6,59	3	1,099

Table 2. Energetic parameters of the equation (1), showing the electronic configuration of parameters in solid, as well in liquid and gaseous states

Element	Phase	A	B	R
Fe	S[3]	-1909	2,528	1,0000
	L, G	-1005	1,941	1,00000
Si	S[3]	-912	1,871	1,0000
	L, G	-721,2	1,526	0,99999
Mn	S	-2378,2	2,6659	1,00000
	L, G	-3258	2,149	1,00000
Ni	S	-341,6	2,2787	—
	L, G	-1648	2,341	1,00000
Cr	S	-935,2	1,9052	—
Al	L, G	-724,9	1,182	1,00000

Table 3. Correspondence of elements electronic configuration parameter to temperatures of their changes in liquid and gaseous state according to the equation (1).

Typical point	Element.									
	Iron.		Silicon.		Manganese.		Nickel.		Aluminum.	
	t, °C	a(T)	t, °C	a(T)	t, °C	a(T)	t, °C	a(T)	t, °C	a(T)
Crystallizing.	1539	4,00	1414	3,00	1244	1,00	1453	4,00	660,5	1,50
Boiling	2750	5,00	2355	3,50	1962	2,00	2732	6,00	2467	2,50
T critical.	6477	6,00	4886	4,00	5777	5,01	6021	8,00	8377	3,00

* — temperatures are taken from [4].

manganese, nickel and aluminum, shown in the equation (1) (Table 2 and 3, Fig. 2).

The atomic electronic configuration parameter for liquid and gaseous state was supposed to be proportional to whole numbers at melting, boiling temperatures and critical temperature, above which the steams of the element can not be condensed by means of volume compression (Table 3). The correlating coefficient value testifies, as well as for solid iron, silicon and manganese, the dependence functionality. The obtained parameter for liquid and gaseous phases should be according to its nature classified (like the analogous parameter for the solid state) as the electronic configuration, as at the critical temperature for mentioned elements obtained parameter is equal to the total quantity of their external electrons.

As qualitative confirmation of abnormally low value a(T) for manganese at the temperature of steel-melting processes in comparison with iron, silicon, nickel and aluminum, we can see abnormal pressure of manganese steam [5]. I. e. the relatively permanent energy influences the less quantity of manganese atoms and, correspondingly, the greater quantity of atoms turns into steam. Lower temperatures of melting and boiling, as well as steam heat of manganese were previously asserted among d-elements of the 4th period of Mendeleev's table owing to assumption of relatively low concentration of collective electrons [6], being confirmed by relatively low a(T) value for manganese in liquid state, approximating to the melting point. This fact also results the stepwise increasing of ferrite quantity in the austenitic high-chromium manganese metal owing to drop of its charge over the manganese melting temperature.

As the quantitative confirmation of obtained electronic-configurational data for solid and liquid state we adduce the comparison of calculated on their base melting enthalpies and entropies according to (3) and (4) with empiric atomic values (Table 4).

$$\Delta S_{melt} = -(B_L - (B_S - \ln X)) \cdot R \cdot 2 \quad (6)$$

$$\Delta H_{melt} = |A_L - A_S| \cdot R \cdot 2 \quad (7)$$

By calculation of melting entropies for silicon not taking into account in the melting energies forming the liquid state parameters can testify the absence of orbital interactions in the molten silicon; this fact is confirmed with the data regarding full destruction of directed links during silicon melting process [6].

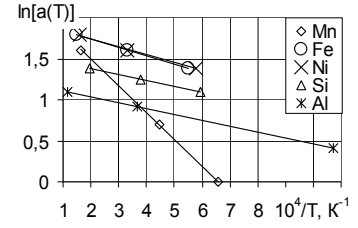


Fig.2 Dependence of parameter of electronic configurations of elements in liquid and gaseous state on the temperature.

Table 4. Comparative values of melting entropies (S) and enthalpies (H).

Element	Bs	B _L	X*	ΔS _{solv} ,	ΔS _{empir} [7]	Δ, %	As	A _L	ΔH _{solv} ,	ΔH _{empir} [7]	Δ, %
				Joule/mole·K.					Joule/mole.		
Fe	Bs	B _L	4,36/4	8,340	8,383	0,5	As	A _L	15091	15190	0,7
Mn	Bs	B _L	(2,67/3) ^{1/2}	9,570	9,657	0,9	As	A _L	14626	14640	0,1
Ni	—	—	—	—	—	—	As·√3	A _L	17556	17610	0,3
Si	Bs	0	(3,5/3) ^{1/2}	29,82	30,05	0,8	—	—	—	—	—

* X – is the expression of elements electronic configuration parameters for elements in the solid state in the nearest to the melting temperature allotropic change and its nearest stable (whole) value.

The electronic configuration parameters for nickel and chrome in the solid state are obtained by determining of solubility in the high-chromium austenitic metal.

The dimension of j-element orbitals, volume increment of all electronic orbitals and pores volume is determined analogously to the iron using equations (2), (4) and (5) correspondingly with the insertion of corresponding parameter of j-element electronic configuration.

We will describe the nitrogen solubility in ferrite and austenite of the high-chromium metal with the dependence analogous to the pure solid iron, taking into account the basic components, i. e. iron, chrome, manganese and nickel and deducing to their concentration the dimensional and electronic factors:

$$[N]_{faz}^{Fe} = V_{PIN,(Fe)T}^{\frac{0,6}{r}} \cdot E_J^{faz} \cdot \frac{100}{10 \cdot A} \cdot \frac{14}{A} \cdot E_N^{faz} \cdot \frac{2 \cdot \sqrt{2}}{\sqrt{3}} \cdot \frac{[Fe]^2 \cdot A^2}{55,8^2} \quad (8)$$

$$[N]_{faz}^j = V_{PIN,(j)T}^{\frac{0,6}{r}} \cdot E_j^{faz} \cdot 100 \cdot \frac{14}{A} \cdot E_N^{faz} \cdot x_j \cdot \frac{[j]^2 \cdot A^2}{A_j^2} \quad (9)$$

where j – mass concentration of the j–element;

55,8 and A — average atomic weigh for iron and steel, g;

A_j – atomic mass of the j–element;

E_N^{faz}, E_j^{faz} – quantity of electrons for different phases (for nitrogen in the ferrite - 1 and in the austenite – 3, for Cr in ferrite - $E_{Cr}^{ferrit} = [a_{max.Fe} - a_{Cr}(T)]$, and for j-element in austenite - $E_j^{austenit} = [a_{max.j} - a_j(T)]$)

x_j –nitrogen solubility structural coefficient, caused by j–element.

The nitrogen solubility in austenite and ferrite of high-chromium steel N_a was found as sum:

$$[N]_{faz} = [N]_{faz}^{Fe} + [N]_{faz}^{Cr} + [N]_{faz}^{Ni} + [N]_{faz}^{Mn} \quad (10)$$

Experimental values of nitrogen solubility in the high-chromium steel and comparative solubility calculated values according to the Taylor series expansion of chrome, manganese and nickel influence up to the parameters of the second order and double parameters are taken from works [8,9] (Fig. 3). For solubility determining we restrict ourselves to 11 austenitic high-chromium steels at temperatures 1200 и 1300°C with chrome content (16,2-18,0%), nickel content (up to 14,6%) and manganese content (up to 16,5%), as well as 4 compositions of ferritic high-

chromium (16,8; 22,6; 24,1; 31,6%weigh) steels at temperatures 1250, 1300 and 1350°C.

The search of solubility dependence was carried out by minimization of the square deviations sum of experimental and calculated values according to the formula (10). The coefficients A, B for chrome and nickel obtained using the equation (1) and x_j obtained using the equation (9), specified in tables 2 and 5 correspondingly apparently demonstrate the vector sum of interactions of alloying elements masses with iron and nitrogen.

As the calculation using the formula (10) is based on physical nature of the nitrogen-into-steel introduction process, we obviously should extrapolate this formula out of the temperature range 1200 up to 1350°C. The major importance has the calculation of solubility at the liquidus temperature for determining of maximum nitrogen alloying level of the liquid bath with nitrogen with the goal to prevent nitrogen porosity during crystallizing.

The check of formulas complexes was carried out during horizontal centrifugal casting of the experimental metal, grade 03X18H5AГ4 (Table 6) into the tube $\varnothing 103 \times 35 \times 1000 \text{mm}$ under elevated

pressure, stipulated by production process [10]. The casting was carried out into the water-cooled horizontal metal mold with coating of lunckerite 2mm thickness at the mold rotation speed 1800rpm.

The experimental steel in the marking beaker was

crystallizing not within the limits of determination of coefficients for provided solubility model in single-phase areas of ferrite and austenite, but in their two-phase area and, being cast under normal conditions, was 1,5% “full grown” in its volume. But by this method of casting the base tube metal on the depth of 10mm from the outside surface was dense unlike the metal intended to mechanical removal by 10mm deep boring from the internal surface for removal of unavoidable technological shrink porosity according to the calculated depth of its occurrence. In the cast under normal conditions billet the sum of its volume enlargement being 1,4% and 3% of pipe

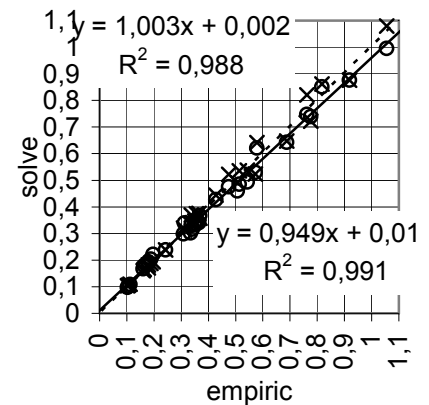


Fig. 3 Convergence of nitrogen solubility in austenite and ferrite.
 O, «—» — $[N]_{\max[Taylor]}$ (R=0,995);
 ×, «- - -» — $[N]_{\max(10)}$ (R=0,994)
 points – reference data,
 lines – correlative right lines.

Table 5. Equation coefficients (1)

Эле- мент	x_j for austenite	x_j for ferrite
Fe	$\frac{2 \cdot \sqrt{2}}{\sqrt{3}}$	1
Cr	$8,06 = \frac{3 \cdot (55,85 - 52)}{\sqrt{2}}$	3 (Cr<20%) $3 \cdot \frac{\sqrt{3}}{2} = 2,60$ (20%<Cr<30%) $2 \cdot \sqrt{2} = 2,83$ (Cr>30%)
Mn	$2,7 = 3 \cdot (55,85 - 54,9)$	—
Ni	$-7,53 = 3 \cdot \frac{\sqrt{3}}{2} \cdot (55,85 - 58,7)$	—

Table 6. Chemical composition of centrifugal-cast steel 03X18H5AГ4 in liquid state, %weigh.

C	N	Cr	Ni	Mn	Si
0,03	0,24	17,9	4,85	4,32	0,38

cavity correspond to the Mendeleev-Clapeyron equation (11) under pressure 625atm and r(P) being amounted to 1. This fact confirms the truth of the formula (3):

$$101325Pa \cdot 625at \cdot \frac{m_{Me} \cdot 0,044}{7850kg/m^3} = \frac{m_{Me} \cdot (0,24\% - 0,17\%) \cdot 100}{0,028kg/mole} \cdot 8,31 \frac{joule}{mole \cdot ^\circ K} \cdot (273 + 1440)^\circ K \quad (11)$$

In the developed steel 03X18Г5АН4 at the calculation temperature solidus 1440°C the calculated nitrogen solubility level (Fig. 6) for austenite and ferrite is correspondingly 0,187% mass and 0,110%mass; this fact allowed to evaluate the truth of adduced calculations regarding nitrogen content in the tube metal and its solubility in 0,17% (Fig. 7), during correction of which, according to the Siverts law, with regard to the elevated pressure in the solid metal, caused by centripetal acceleration of being still liquid 10mm layers in the rotating mold the fracture was observed at the nitrogen actual content curves, Fig.7. In addition, proceeding from the nitrogen solubility values at the crystallization temperature in the steel 03X18Г5АН4 and in its austenite and ferrite, the quantity of ferrite at the crystallization temperature was calculated, being 25%rel.

3. Deductions: The nitrogen solubility in steel depends only on its electronic-configurational energetic interactions while its structural factors as crystallographic directivity and dimensional factor of the Hume-Rothery's principle are derivative from it, as well as heat capacity, electrical resistance, heat conduction, not described in this article.

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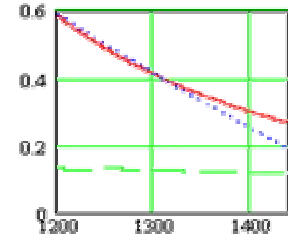


FIG. 4. Nitrogen solubility in austenite and ferrite in steel 03X18H5AG4, %weigh.

«.....»- austenite acc. to (15);
«-->» -ferrite acc. to (15);
«-->» - austenite acc. to the Taylor series expansion

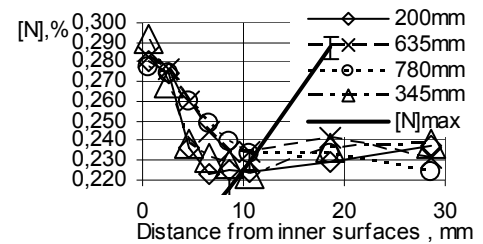


Fig 5. Content of nitrogen in centrifugally cast tube steel grade 03X18H5AG4 and his solubility by an action centripetal forces, %weigh.

Numbers on a figure – distance from pouring end, mm;

«-->» - maximally solubility in steel on thickness of tube by pressure in liquid an action centripetal forces from solubility in normal conditions 0,17%weigh.