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Optimization of nitride-forming elements additions into steel

To improve quality of steel the small amount of nitride-forming elements, such as vanadium, niobium, aluminum, titanium, zirconium is added during melting. Usually, the addition of nitrogen is not required, since steel already contains sufficient amount of nitrogen. However, in some cases, nitrogen is added as an alloying element.

The optimum addition of nitride-forming elements leads to the formation of highly dispersed nitrides, which, in turn, provides grain refinement, grain-boundary pinning, hardening without loss of plasticity, improvement of impact toughness and reduction of fracture appearance transition temperature. These effects are known for a long time and they are commonly used in industry [1].

It must be emphasized that the extension of this progressive method to the new grades of steel is made difficult by the fact that the selection of optimum amount of nitride-forming elements is done empirically, thus demanding laborious and expensive industrial trials.

The technique of preliminary estimate of optimum concentration of nitride-forming elements in various grades of steel [2, 3] has been developed in the Moscow Institute of Steel and Alloys. The purpose of calculation is to decrease the quantity of experimentally studied compositions and consecutive reduction of needed recourses for research trials. Such calculations are based on available past experimental research on empirical optimization of additions of nitride-forming elements in steel.

The central assumption of the technique is that only nitrides of favorable sizes, shape and other characteristics defined by the temperature of formation of nitride phase (more precisely, a temperature of the beginning of its precipitation from a solution during cooling) improve the quality of steel. It is apparent, that if the temperature of the beginning of nitride formation is too high, one can expect the excessive coarsening of the precipitate, which will negatively affect the plastic properties. On the other hand, if the temperature of nitride formation is too low, the process of precipitation might not develop properly and not give the expected beneficial effect.

The calculation of a real temperature of the start of nitride-formation in steel is complicated by difficulty of taking into account all influencing factors. This difficulty can be overcome if one accepts as a defining parameter the calculated thermodynamic (not real) temperature of the beginning of nitride-formation i. e. the temperature wherein the nitride formation during cooling of steel with nitride-forming microalloying elements becomes thermodynamically possible.

If the value of such temperature is approximately identical for various grades with the optimum (empirically defined) concentrations of nitride-forming elements, it will be accep-

ted as optimum temperature of the beginning of the nitride-formation (T_{RNopt}). Once the above temperature is known, the reverse calculation can give the optimum concentrations of nitride-forming elements for other steel grades (with different alloys). The accepted assumptions are of little consequence at such double calculation (direct and reverse) since inaccuracies associated with these assumptions will cancel each other.

The basic principles and one of variants of the a procedure for calculation of nitride-forming temperatures in steel grades of various compositions are presented [2], and some results (including values T_{RNopt}) listed in [3]. Reference [3] also contains an example of the estimation of optimum concentrations $[R]$ and $[N]$ for one of the grades where experimental data is not available.

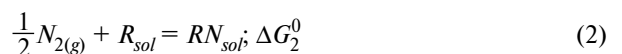
The current work presents the results of new calculations performed following the same principles, described in [2, 3], but with application of somewhat different calculation procedure and more precise thermodynamic data. In particular, the use of the refined value of, has allowed to get a value of T_{VNopt} closer to reality. In addition, the calculations now can be performed by using the specially developed software located on site <http://maresias.msk.ru/>.

The calculation procedure of the thermodynamic temperature of the beginning of the nitride-formation is the following:

The chemical equation of the formation of a nitride is



In order to find temperature dependence of the standard Gibbs energy of reaction (1), equation (1) can be presented as sum of the following reactions¹:



The temperature of the nitride-formation can be found from the equilibrium constant of the reaction (1)

$$\ln K_1 = -\frac{\Delta G_1^0}{RT} = \frac{1}{f_N \cdot [N] \cdot f_R \cdot [R]} \quad (5)$$

¹ If phase states of the pure nitride-forming element and the solution is not same at the sought temperature of the beginning of the nitride-formation, it is required to consider a energy of melting in addition

Table 1. Values of standard Gibbs energy of reactions used in calculations

Chemical equation	$\Delta G^0 = A + B \cdot T$, Joule/mol	
	A	B
$1/2 N_2 + V_{sol} = VN_{sol}$	-207500	78
$1/2 N_2 + Ti_{sol} = TiN_{sol}$	-334500	93
$1/2 N_2 + Al_{liq} = AlN_{liq}$	330000	117
$1/2 N_2 + Zr_{sol} = ZrN_{sol}$	360200	90
$[V] = V_{sol}$	42300	29,2
$[Ti] = Ti_{sol}$	69500	27,28
$[Al] = Al_{liq}$	62800	23,8
$[Zr] = Zr_{sol}$	80300	34,9
$[N] = 1/2 N_2$	-10500	-20,37

Table 2. Temperature dependences of interaction parameters of nitrogen in iron-based melts accepted in calculations [5]

Element	A	B	C	D	$e_{N,1873}^R$	$r_{N,1873}^R$
Al	-293,6	0,093	50,9	-0,022	-0,063	0,0051
B	731,7	-0,292	68,2	-0,036	0,099	0,0009
C	216,1	-0,018	37,0	-0,012	0,097	0,0077
Cr	-230,8	0,076	2,9	-0,001	-0,048	0,00032
Mn	72,9	-0,065	-10,8	0,006	-0,026	0,00029
Mo	31,3	-0,024	-2,1	0,001	-0,0071	-0,00018
Nb	-284,9	0,073	31,3	-0,014	-0,079	0,00245
Ni	54,8	-0,019	-0,9	0,00045	0,010	-0,00001
P	3,13	0,030	10,8	-0,00205	0,031	0,0037
S	9392	-5,08	-8386	4,53	-0,066	0,0521
Si	145,6	-0,035	-37,5	0,021	0,043	0,00063
Ta	-243,3	0,091	18,3	-0,009	-0,038	0,00064
Ti	30891	-16,9	-57137	30,7	-0,391	0,166
V	-303,9	0,058	4,64	-0,0013	-0,100	0,0012
W	-116,3	0,053	11,3	-0,005	-0,009	0,0005

To find the temperature dependence of the activity coefficient of a nitride-forming metal, one can use the theory of quasiregular solutions:

$$\ln f_i = \frac{1873 \cdot (\tau - T)}{T \cdot (\tau - 1873)} \cdot \lg f_{i(1873)} \quad (6)$$

which, according to [4], gives more precise results than the theory of regular solutions often used for this purpose.

Wagner's formalism of the second order can be used for the calculation of the activity coefficient of nitrogen:

$$\lg f_N^{alloy} = \sum_{i=1}^n e_{N(i)}^R [\%R] + \sum_{i=1}^n r_{N(i)}^R [\%R]^2 \quad (7)$$

The data used in calculations are presented in Tables 1, 2.

The values of interaction parameters and the data on standard Gibbs energy for the majority of elements are accepted according to [4]. To extrapolate the interaction parameters of nitrogen to different temperatures the improved temperature dependences of parameters of 1st and 2nd order were used. These relationships were found in [5] by statistical processing of the data base specially created and containing all known results of experimental measurements — 2776 values of solubility of nitrogen in iron-based melts. Later the results of [5] have been corrected slightly by A. Dalmatov (several additions processed using Statistica up-to-date package have been included in the data base). Undertaken comparative calculations have shown that the received improved dependences gave the best agreement between calculated and experimental results. The authors are not aware about any new works for generalization of data about thermodynamics of nitrogen solutions in iron-based melts.

Values of T_{RNopt} for various nitrides and steel grades, estimated by using data on optimum concentration of nitride-forming elements $[R]_{opt}$ and $[N]_{opt}$, are presented in table 3. Table 3 shows the average values of T_{RNopt} and confidence intervals ($\pm \sigma$) of T_{RNopt} for each of the nitrides. The thermodynamic temperatures T_{RNopt} for the grades not listed in Table 3 should fall within the calculated confidence interval ($\pm \sigma$) with a 68 % probability.

The results of calculation in table 3 show that the values of T_{RNopt} vary much less within the limits of one nitride, than the values of optimum concentrations of $[R]_{opt}$ and $[N]_{opt}$.

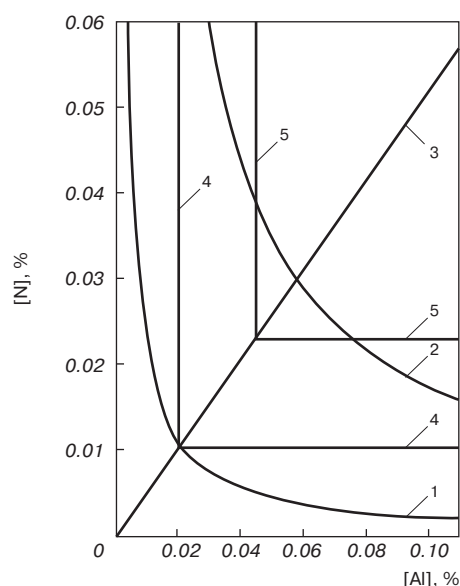


Fig. 1. The example of calculation of optimum concentration of aluminum and nitrogen in steel 30HGSA (explanations in the text)



Fig. 2. Working window of the program of calculation of optimum concentration of nitride-forming elements in steel

You have defined the composition

- C: 0.3
- Si: 1
- Mn: 1
- Cr: 0.8
- S: 0.025
- P: 0.025
- Cu: 0.15
- Ni: 0.2
- As: 0
- Mo: 0

Nitride-forming element: Al

Optimal temperature of beginning of nitride-forming 1279.29 C

[Al], %	[N], %
0.01	0.0716762421545
0.06	0.0119025511916
0.11	0.00652785658691
0.16	0.00451420469898
0.21	0.00345944683488
0.26	0.00281010864321
0.31	0.00236993534109
0.36	0.00205173933897
0.41	0.00181087625908
0.46	0.0016221175541

Fig. 3. Results of calculation of optimum concentration of a nitride-forming element

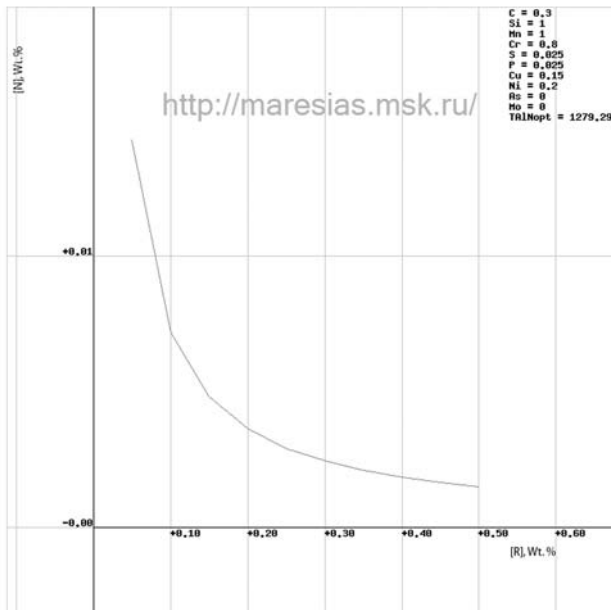


Fig. 4. Relationship of $[N]_{opt}$ and $[R]_{opt}$, derived as the result of the performed calculation (the example for AlN)

These thermodynamic temperatures (T_{RNopt}) are essentially independent of up steel grade and other factors. This enables us to deem acceptable the assumption of the current work that the beneficial effect of nitrides is largely defined by thermodynamic temperature of their formation. Such conclusion makes it possible to estimate, at least roughly, optimum concentration of nitride-forming elements in steel using an average optimum thermodynamic temperature of a formation of a concrete nitride as an invariant.

The results of a reverse-calculation — the prediction of optimum concentration of [Al] and [N] for a steel 30HGSA using of the calculated value, $T_{AlNopt} = 1304 \pm 48 \text{ }^\circ\text{C}$ are presented on Fig. 1.

The area between two isotherms — hyperboles related to 1352 and 1256 $^\circ\text{C}$, is a sought-for field of optimum concentration of nitride-forming elements. The points for experimental trials should be selected within this area.

As mentioned earlier above, the calculation of isotherms of a nitride-formation and construction of the graph can be done using the site <http://maresias.msk.ru>/Fig. 2). For this purpose it is necessary to enter into the program data about steel composition, then to choose a nitride-forming element and to calculate values of optimum concentration.

In doing so, the optimum temperature of nitride-formation will be automatically chosen as average calculated temperature of nitride-forming. For those users who have calculated the more refined temperature of nitride-formation independently, there is an option to use their own value of T_{RNopt} .

Table 3. Experimental values of optimum concentration of nitride-forming elements in some steel grades and thermodynamic temperatures of nitride formation calculated on them and maximum possible quantities of nitride phases

Steel type	[R] opt	[N] opt	Topt	Quantity of RN, mol/t	Steel type	[R] opt	[N] opt	Topt	Quantity of RN, mol/t
Zirconium nitride					Vanadium nitride				
(100) GS	0,115	0,015	1431	11	20G2D	0,130	0,020	1066	14,2
10HGS	0,070	0,010	1458	7	20G2M	0,150	0,020	1078	14,2
40HN	0,090	0,010	1442	7	12HM	0,360	0,015	1104	10,7
35HN	0,090	0,010	1446	7	St10	0,060	0,010	970	7,1
R6M3	0,065	0,025	1420	7	1010HG2D	0,080	0,015	997	10,7
R6M5	0,100	0,076	1517	11	80H4GSM	1,040	0,070	1388	—
17H19M2	0,017	0,100	1340	—	20H21SN3M2	0,460	0,008	912	5,7
Average value $T_{opt} \pm \sigma$ 1436 \pm 48,7					30H2NM	0,150	0,035	1120	25
Aluminium nitride					(150) H5M5S	5,000	0,050	1595	—
15G2	0,080	0,015	1325	11	(130) R6M6K6S	2,500	0,045	1466	—
15G2	0,031	0,016	1263	10	07H18G12N5	1,400	0,050	1024	—
15G2	0,060	0,025	1342	17	55H15G20	1,000	0,300	1126	—
10G2	0,250	0,008	1341	6	35H19N4G15	1,450	0,310	1140	—
18G2	0,040	0,010	1244	7	03H18N13M3	0,300	0,220	1224	—
20HГ	0,065	0,023	1333	14	(100) H2G12SM	0,600	0,065	1262	—
08U	0,055	0,010	1255	7	Average value $T_{opt} \pm \sigma$ 1116 \pm 58,5				
20HГ2MS	0,036	0,028	1346	13	Nitride of the titan				
22H2G2S	0,045	0,003	1181	17	15G2	0,065	0,021	1488	13,5
12HGN2M	0,070	0,023	1322	16	15G2	0,040	0,038	1496	8,3
40H2N5GSM	0,025	0,026	1299	9	15G2S	0,060	0,011	1434	7,8
05H13N8M2	1,100	0,010	1511	—	20G2S	0,035	0,015	1414	7,3
10H17	0,100	0,010	1315	—	(100) GS	0,115	0,015	1510	10,7
10H17	0,060	0,020	1166	—	St20	0,067	0,010	1429	7,1
Average value $T_{opt} \pm \sigma$ 1304 \pm 48					St35HM	0,090	0,010	1452	7,1
Vanadium nitride					30HGS	0,090	0,010	1455	7,1
15G2	0,125	0,025	1084	18	40NN	0,090	0,010	1454	7,1
15G2	0,160	0,023	1094	15	20HGNM	0,060	0,010	1416	7,1
15G2	0,120	0,020	1064	14	(135) H	0,350	0,010	1519	7,1
16G2	0,100	0,023	1048	16	01H17	0,415	0,008	1371	—
20G2	0,120	0,005	962	4	01H17	0,260	0,010	1416	—
10G2S	0,100	0,015	1026	11	01H18	0,160	0,008	1374	—
20G2S	0,090	0,016	1043	11	01H18M2	0,200	0,006	1359	—
70G2S	0,120	0,018	1109	13	01H17G2	0,220	0,010	1404	—
10GCD	0,130	0,023	1091	16	01H18G2	0,200	0,008	1375	—
02G4	0,170	0,025	1070	18	03H19M2	0,240	0,010	1416	—
04G4S	0,110	0,019	1030	14	04H12N5GS	0,290	0,009	1416	—
60GS2	0,300	0,010	1136	7	01H26	0,160	0,025	1465	—
20G2S	0,080	0,015	1021	11	90G10	0,300	0,018	1555	—
					R6M6K8	0,090	0,045	1607	—
					Average value $T_{opt} \pm \sigma$ 1447 \pm 27,8				

Results of calculation of optimum temperatures using this site are presented in on Figures 3 and 4.

The results of the calculation show that values for nitrogen and aluminum fall within the area of the values presented on Figure 1.

Some limits of the area of recommended optimum concentrations can be set based on the consideration of a limited quantity of formed nitride phase. The approximate assessment of quantity of nitride phase in low- and medium alloy steels can be done with the assumption of full transition of either nitrogen or a nitride-forming element to nitride. The results of such assessment of optimum quantity of a nitride phase in various steels are presented in Table 3. As is it seen from the table, the optimum quantities of nitride phase for various steels, expressed in mol/t, are relatively in close proximity. In case of aluminum nitride the interval of $gAlNopt$ is from 7.22 to 15.68 mol/t. The area corresponding to this interval is limited

by lines 4 and 5 on Figure 1. Thus, the area limited by isotherms 1 and 2 and lines 4 and 5 is the area of optimum concentration of aluminum and nitrogen in a steel 30HGSA where it is possible to expect formation of beneficial nitrides.

State-of-the-art methods of the analysis allow carrying out a correction of a content of a nitride-forming element [R] on heat to heat basis, if necessary. To do this requires the express analysis of nitrogen in metal, determination of the content of [R]_{opt} corresponding to the analyzed nitrogen and specific additions of nitride-forming metal during the ladle treatment.

It is expedient to use practically the described method at the plants, not only for the forecast of optimal technological additives of nitride-forming elements in different steels, but also for analysis of large information massifs such as “composition — property”, in order to reveal causes of off-grade metal, improvement of metal quality etc.

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The method of calculation of the kinetics of metallurgical processes at produce of ferrous metals

In the present article we try to formulate a unified approach to the question of the transposition of the kinetic equations of various degrees of complexity which describe the kinetics homogeneous and heterogeneous chemical processes, which take place in the metallurgical equipment of the ferrous industry. As the simplest universal method one can use the simplex method, whereby a kinetic curve equation is transposable to a dimensionless form by the use of analog simplexes corresponding to several values of c_i and τ_i which are chosen from the experimental kinetic curve (where c_i is the concentration of the reacting component at instant τ_i) [1–8]. Thus, for example, for any two values c_i and c_{i+1} corresponding to instants τ_i and τ_{i+1} and located on the experimental kinetic curve and, provided that the kinetic equation is transposed to the form $\tau_i = f(c_i)$, we can write: 1) for instant τ_i , $\tau_i = f(c_i)$; 2) for instant τ_{i+1} , $\tau_{i+1} = f(c_{i+1})$.

In the case of the relevant time interval $\Delta\tau_i$, the form of the functional dependence of $\Delta\tau$ and S_i on c_i and c_{i+1} is determined by:

$$\Delta = \tau_{i+1} - \tau_i = \varphi_1(c_i; c_{i+1}), \quad (1)$$

$$S_x = \tau_{i+1}/\tau_i = \varphi_2(c_i; c_{i+1}). \quad (2)$$

The simultaneous solution of the equations $\Delta\tau_i = f(c)$ and $S_i = f(c)$ makes it possible to derive the criterion relationship describing the kinetics of the chemical process being studied. The possibility of using the simplex method to transpose kinetic equations describing the kinetics of homogeneous and heterogeneous processes to the dimensionless form is illustrated by the examples set out below.

1. The kinetic equation describing the kinetics mechanism of simple nth (where $n=0$) order reactions has the form:

$$\frac{c}{c_0} = 1 - k_0 \frac{\tau}{c_0}, \quad (3)$$

where m is the order of the reaction, k_0 is the reaction rate constant, c_0 and c_i are, respectively, the initial and instantaneous concentrations of the reacting component, $\tau_i = 0$ and τ_i is the time.

The values of the reaction rate constant can be calculated from the equation

$$-\frac{\Delta c}{\Delta \tau} = k_0. \quad (4)$$

2. The kinetic equation describing the kinetics mechanism of simple nth (where $n = 1$) order reactions has the form:

$$\frac{c}{c_0} = \exp(-k_1 \tau), \quad (5)$$

where k_1 is the reaction rate constant (where $n = 1$).

$$\Delta \tau = (1/k_1) \ln S_c^{-1}, \quad (6)$$

$$\Delta c = c_0 = (S_c^{S_\tau/S_{\tau-1}} - S_c^{1/S_{\tau-1}}) \quad (7)$$

and

$$-\frac{\Delta c}{\Delta \tau} = k_1 c_0 (S_c^{S_\tau/S_{\tau-1}} - S_c^{1/S_{\tau-1}}) / \ln S_c. \quad (8)$$

3. The kinetic equation describing the kinetics mechanism of simple nth (where $n > 1$) order reactions has the form:

$$\frac{c}{c_0} = \left(\frac{1}{1 + (n-1) k_n c_0^{n-1} \tau} \right)^{1/(n-1)}, \quad (9)$$

where k_n is the reaction rate constant (where $n > 1$)

$$\Delta \tau = [1/(n-1) k_n c_0^{n-1}] \frac{(1 - S_c^{n-1})(S_\tau - 1)}{S_\tau S_c^{n-1} - 1}, \quad (10)$$