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THE ROLE OF TAKING INTO ACCOUNT THE INTERATOMIC INTERACTION IN PREDICTING THE COMPLEX OF STRUCTURALLY-SENSITIVE PROPERTIES OF STEELS AND ALLOYS FOR SPECIAL PURPOSE

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The aim of the work is to identify the influence of the chemical composition of steels and special-purpose alloys on the formation of their physicochemical and structural-sensitive properties. This problem is solved by mathematical modeling of the inseparable chain «composition - structure – property» taking into account the parameters of interatomic interaction in the melt based on the concept of a directed chemical bond. A steel melt is considered as a chemically homogeneous system, and the state of the melts is expressed through a set of integral parameters, the main of which are: Zy - system charge state parameter (e); r - statistically average internuclear distance (10-1nm); tgα is a constant for each element, which characterizes the change in the radius of the ion as its charge changes. On the basis of experimental information on properties and using the parameters of interatomic interaction, computational models are proposed for predicting the properties of steels and alloys. The forecast models took into account the parameters of micro-inhomogeneity of steel, which ensured a high accuracy of the operational forecast. A comparative analysis of the results of steel melting with the corresponding calculations based on the JMatPro software package confirmed the effectiveness of using the interatomic interaction parameters as models. The proposed models for determining the melting of chromium-nickel steels are recommended for use with the content of basic elements Cr, Ni from 0 to 30%. The research results are recommended for use in industrial environments through the integration of the developed models in the process control system of steelmaking, which will contribute to the directed formation of the composition and properties of smelting products, as well as reducing energy costs.

Keywords: special steels, interatomic interaction parameters, physicochemical properties, micro-inhomogeneity, predictive models

The state of the problem. In recent years, the tendency to increase the demand for high-quality metal products has become more pronounced. The depletion and deterioration of the quality of mineral resources, both in the world market and within our country, puts on the agenda a search for new approaches and the improvement of the adopted technological solutions aimed at improving the quality of special-purpose steels and alloys, which is associated with physical and chemical modelling of metal melts and their interactions in the «metal-slag» system. This will provide a theoretical basis for a scientifically-based choice of rational modes of melting special-purpose steels, as well as the efficient use of raw materials and energy resources.

Prediction of a complex of physicochemical (melting and crystallization temperature, density, micro-inhomogeneity, viscosity, surface tension,

electrical conductivity and other properties) of the mechanical and operational properties of steels and alloys of special value, will allow you to quickly manage the process of refining the steel in the ladle, as well as the processes during casting and crystallization, and improve the technical and economic indicators of smelting.

Despite the growing amount of research on these issues, there are still difficulties in predicting the structure-sensitive properties of metallic multicomponent melts, which is largely due to the lack of the formulated fundamental positions of the liquid state of metallic systems that would serve as the basis for the formation of the generally accepted structure.

Currently, the most actively developed and used to explain the physicochemical and structural features of liquid metal systems are ideas about their microheterogeneous structure, which are partially reflected in the works [1–5]. Segregation of clusters in steel violates the homogeneous state of the melt, as the most important indicator of quality [6], viscosity increases and may cause the formation of non-metallic inclusions and, as a result, defects in the finished metal product, thereby reducing the performance and service life of the product.

Differences in the forces of interatomic interaction, describing the physicochemical relationship between the individual components of the melt manifest themselves in their clustering ability (Fig.1).

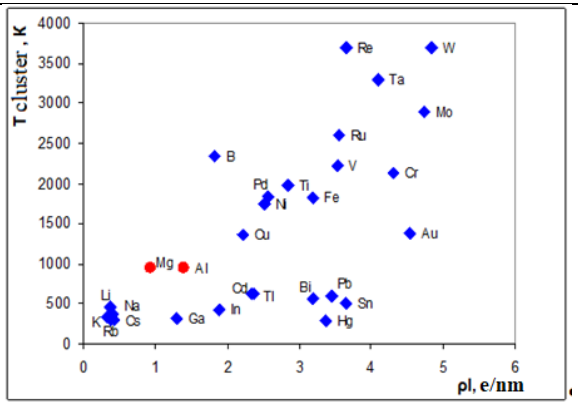


Figure 1 – Dependence of the temperature of existence of a cluster of one-component metal melts on the parameter of the directed charge density (ρ_l) according to [7]

The most stable clusters are formed with the strongest inter-atomic bonds between the components of the melt. From the data in Figure 1 to such should be attributed Re, Ta, W, while the most easily destroyed are K, Na, Li.

Proper consideration of the temperature of the existence of clusters and their destruction is one of the effective technological methods, which will ensure the uniformity of the structure of the metal melt and optimize the temperature of melting.

Purpose of the work – identifying the influence of the chemical composition of target steels on the formation of their structurally sensitive properties based on the interatomic interaction parameters in their melts in order to simulate processes in the metal-slag system when solving problems of a scientifically-based choice of effective alloying additives.

The main research material.

According to many years of experience in predicting the physicochemical properties of metal and slag melts in Z.I. Nekrasov Iron and Steel Institute of NAS of Ukraine, this problem is solved by mathematical modelling of an inseparable «composition – structure – property» chain, taking into account the interatomic interaction parameters in the melt, based on the concept of a directed chemical bond developed by Prikhodko E.V. and which considers the melt as a chemically uniform system [8].

Chemical individuality, reactivity, chemical and structural state of the investigated melts is expressed through a combination of integral parameters, the main of which are: Z^y – system charge state parameter; d – statistically average internuclear distance, 10^{-1}nm; tgα – constant for each element characterizing the change in the radius of an ion when its charge changes.

Additional introduction of the directional charge density parameter (ρ_l, e/nm) allows you to indirectly take into account the microheterogeneity of the melt (clusters, microcrystallites, sibotaxis, swarms). Entering the listed parameters reduces the parametricity of the models and increases their physicality.

The efficiency and effectiveness of this method was confirmed by us in the development of models for predicting the temperatures of melting and crystallization of chromium-nickel steels. [9], iron carbon steels (constructional, instrumental, rail) [10], high-temperature nickel alloys (HTNA) [11], aluminium and magnesium alloys [12] with high forecast accuracy (Table 1). Thus for heat resisting nickel alloys, refractory elements (Mo, W, Re, Ta) allocated in a separate subsystem.

Table 1. Accuracy of predicted models of melting temperatures and crystallization of steels and alloys for special purposes

Metallic melts	Model	Accuracy
Chromium-Nickel steel	T_L, $T_S = f(Z^y, d, tg\alpha)$	$R^2 \geq 0.93$
Iron carbon steels	T_L, $T_S = f(Z^y, \rho l_{общ})$	$R^2 \geq 0.95$
High-temperature nickel alloys	T_L, $T_S = f(\rho l_{общ}, tg\alpha_\gamma)$	$R^2 \geq 0.88$
Aluminium alloys	T_L, $T_S = f(\rho l_{общ})$	$R^2 \geq 0.92$
Magnesium alloys	T_L, $T_S = f(\rho l_{общ})$	$R^2 \geq 0.97$

Here: $tg\alpha_\gamma$ – weighted average parameter of the micro-doping subsystem constants γ-solid solution hardeners (Mo, W, Re, Ta).

The proposed models for determining the fusibility of chromium-nickel steels are recommended for use with the content of basic elements Cr, Ni from

0 to 30%. Developed regression models for iron-carbon steels and alloys are recommended for use when the iron content in the melt matrix (to 97%) and the total alloying component (to 20%). Aluminium and magnesium alloys have a similar model structure, which is due to their location in one area in a micro-inhomogeneous structure (Fig. 1.) and is expressed by the parameter of the directed charge density (ρ_l, е/нм).

All the developed models were additionally tested on independent data that were not included in the initial samples, which confirmed their adequacy and the ability to recommend the results obtained for use in the ASNI system and the process control system.

The developed models were also tested by comparing with the well-known foreign specialized computer complex JMatPro with the assistance of scientists from the Paderborn University (Germany) [13], which confirmed their adequacy for making decisions on controlling the temperature of melting.

Comparative analysis of calculated and experimental data for liquidus and solidus temperatures of iron-carbon steels, aluminium and magnesium alloys agree well with each other in both cases (both when using the concept of directed chemical bonding (DCB) and the JMatPro complex) and are highly predictable.

It should be noted that for sampling these melting points and crystallization of high-temperature nickel alloys there is a significant inconsistency in calculations using the JMatPro program (Fig.2, Table 2).

Table 2. Estimation of the accuracy of the prediction of the crystallization temperature of high-temperature nickel alloys

Alloy grade	T_S exp. °C	T_S by DCB °C	T_S by JMatPro °C
CMSX-10	1394	1396.06	1322
ЖС32	1345	1343	1242
ЖС6К	1265	1281.76	1256
ЖС6У	1275	1272.63	1206
Rene N5	1336	1343.42	1195
Rene N6	1365	1363.79	1174
CM186LC	1337	1345.52	1160
CM247LC	1313	1299.52	1120
PWA 1480	1350	1318.72	1116
CMSX-4	1339	1343.84	1154
CMSX-11B	1287	1284.88	1136
CMSX-11C	1275	1286.86	1156
Forecast error, %		0.66	10.30

In [13], researchers also noted a significant discrepancy when calculating the solidus temperature using the JMatPro software for nickel alloys in particular for CW6MC and N3M alloys is 112 and 177, respectively, which is

probably due to the fact that the content of of alloys for which software was developed based on a modified Shile approximation

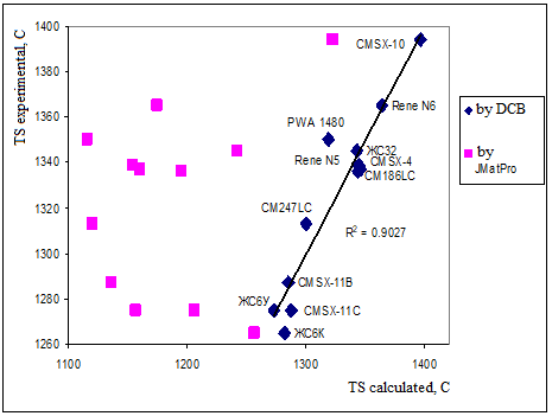


Figure 2. Comparison of experimental and calculated values of solidus temperature of high-temperature nickel alloys according to [14]

As chromium-nickel steels (Table 3), are among the most popular on the domestic and foreign markets steel-smelting production, in this paper the emphasis is on the basic technological properties - their density in liquid and solid state (Figure 3).

Table 3. Fragment of a sample of data on the chemical composition of the investigated steels

Сталь	C	Mn	Si	S	P	Cr	Ni	W	Mo	Cu	Ti	Fe
9Х	0.9	0.3	0.4	0.008	0.012	1.6	0.15	0	0	0	0	96.63
9Х2	0.9	0.3	0.4	0.007	0.013	2	0.15	0	0	0	0	96.23
35ХНЛ	0.35	0.65	0.42	0.016	0.017	0.69	0.79	0	0	0	0	97.067
35ХМЛ	0.37	0.47	0.35	0.019	0.018	0.91	0	0	0.33	0	0	97.533
10Х18Н9ТЛ	0.08	1.14	0.7	0.016	0.012	17.65	8.18	0	0	0	0.3	71.922
15Х25Н19С2Л	0.14	1.22	2.74	0.015	0.014	25.11	18.16	0	0	0	0	52.601
Х25Т	0.07	0.34	0.62	0.008	0.026	25.05	0.35	0	0	0.14	0.72	72.676
20ХН3А	0.205	0.45	0.27	0.025	0.025	0.75	2.95	0	0	0.3	0	95.025
20Х13	0.19	0.22	0.27	0.014	0.012	12.5	0.15	0	0	0.1	0.03	86.514
12Х13	0.12	0.8	0.8	0.025	0.03	13	0.6	0	0	0	0	84.625
30Х13	0.275	0.8	0.8	0.05	0.03	13	0.6	0	0	0.3	0.2	83.97
12Х17	0.12	0.8	0.8	0.025	0.035	17	0	0	0	0	0	81.22
12Х18Н10Т	0.09	1.22	0.4	0.007	0.03	17.85	9.99	0.07	0.09	0.25	0.52	69.483
Х25Т	0.07	0.34	0.62	0.008	0.026	25.05	0.35	0	0	0.14	0.72	72.676
40Х13	0.395	0.6	0.6	0.025	0.03	13	0.6	0	0	0	0	84.75

Thus, the model for predicting the density of chromium-nickel steels is: ρ_L, $\rho_S = f(tg\alpha)$.

According to a similar method for 19 compositions of high-temperature nickel alloys, their most informative parameters were identified - the average internuclear distance $d_{общ}$ and $Z^y_{общ}$ – charge state of the general system of the corresponding alloy. Since for high-temperature nickel alloys it is especially

important to maintain long-term high-temperature operation of products, which is ensured by alloying with refractory elements, the effect of $tg\alpha_\gamma$ – of the weighted average parameter of the micro-doping subsystem constants γ – solid solution hardeners (Mo, W, Re, Ta, Ru). With this approach to density modeing, it is described by the equation (1):

$$\rho = -47{,}26+18{,}54d_{общ}+13{,}75tg\alpha_\gamma+1{,}09Z^{y}_{общ} \quad R^2 \geq 0.75 \qquad (1)$$

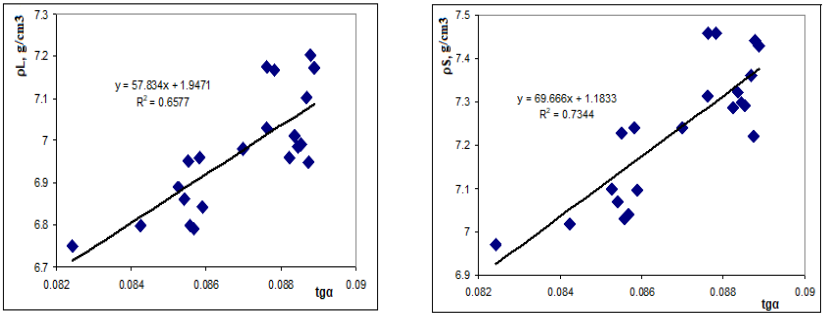


Figure 3. The dependence of the density of chromium-nickel steels during melting and crystallization of the weighted average parameter tgα

The developed model for predicting the density of heat-resistant nickel melts was additionally examined on independent data. [15, 16, 17], which confirmed its performance. Along with the above physicochemical properties of special-purpose steels and alloys, we studied the possibility of predicting an important structural-sensitive characteristic of alloyed chromium-containing steels in the temperature range 1600-1750 °C - viscosity (Table 4).

Table 4. The parameters of interatomic interaction of the studied steels

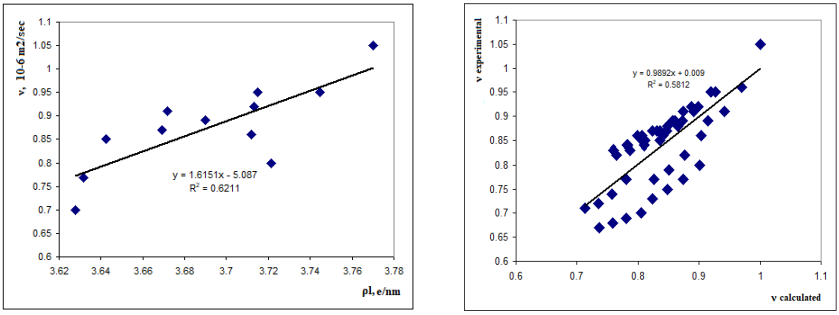
Steel	**Z^y, e**	**d, 10^{-1}nm**	**tg α**	**ρl, e/ nm**
X9C2	1.536939	2.7334	0.086388	3.711785
2X13	1.586772	2.7588	0.085499	3.721357
X6C	1.399612	2.7535	0.087248	3.631676
50C2	1.28208	2.7031	0.088718	3.627713
X18H25	1.903133	2.7515	0.088927	3.642391
X18H12	1.826277	2.7919	0.086539	3.66897
X18H9	1.80275	2.7887	0.086025	3.689942
2X18H9	1.776506	2.783	0.085543	3.713191
X17H2	1.692633	2.7863	0.084424	3.744633
P18	1.561596	2.7347	0.086102	3.770002
P9	1.444351	2.7178	0.087228	3.714686
7X3	1.332615	2.6946	0.088322	3.671608

Knowledge of the viscosity characteristics of metal melts allows us to scientifically-based approach to the choice of injected alloying additives in steel, as well as to regulate ion-exchange and heat-mass transfer processes in the metal-slag-additive system.

Analysis of the relationship between the parameters of interatomic interaction with the kinematic viscosity of steels made it possible to establish that taking into account the directional charge density allows linearization of the dependences, which is due to the influence of micro-inhomogeneous regions, in particular clusters of refractory elements - tungsten and chromium (Fig.4.a). On the picture - Fig.4.b is shown a comparative analysis of the calculated and experimental data of the kinematic viscosity of alloyed steels of the target value.

Taking into account the temperature factor, the operational predictive model is (2):

$$\nu = f\left[\frac{(-12{,}0647 + 2{,}832\rho l + 34{,}692 tg\alpha)}{T \cdot 10^3}\right] \qquad R^2 \geq 0.6 \qquad (2)$$



a) b)

Figure 4. Dependence of kinematic viscosity on the directional charge density of alloyed steels at 1600°C; b - comparative analysis of calculated and experimental values of kinematic viscosity in the temperature range 1600-1750°C [18]

Conclusions.

In this paper, analytical dependencies are proposed for calculating the melting point, density, and viscosity of metal melts, based on the concept of directed chemical bonding and physico-chemical modelling of melts as a chemically unified system at the level of interatomic interaction.

Accounting for the interatomic interaction parameters (Z^y; d; tgα) and the microinhomogeneity parameter - ρ_l made it possible to improve the accuracy of predictive models.

High agreement of the calculated with experimental data, as well as comparative analysis with calculations for the widely used foreign software package based on the basics of classical thermodynamics - JMatPro confirmed

the adequacy of the obtained models, which allows us to recommend them for use in automated research system and automated process control systems of technological processes of steelmaking.

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И. Р. Снигура, Д. Н. Тогобицкая

Роль учета межатомного взаимодействия при прогнозировании комплекса структурно-чувствительных свойств сталей и сплавов специального назначения

Целью работы является выявление влияния химического состава сталей и сплавов специального назначения на формирование их физико-химических и структурно-чувствительных свойств. Эта задача решается путем математического моделирования неразделимой цепочки «состав - структура - свойство» с учетом параметров межатомного взаимодействия в расплаве на основе концепции направленной химической связи. Расплав стали рассматривается как химически однородная система, а состояние расплавов выражается через совокупность интегральных параметров, основными из которых являются: Zy - параметр состояния заряда системы (е); r - статистически среднее межъядерное расстояние (10^{-1}нм); tgα - постоянная для каждого элемента, характеризующая изменение радиуса иона при изменении его заряда. На базе экспериментальной информации о свойствах и с использованием параметров межатомного взаимодействия предложены расчетные модели для прогнозирования свойств сталей и сплавов. В прогнозних моделях учтены параметры микронеоднородности стали, что обеспечило высокую точность оперативного прогноза. Сравнительный анализ полученных результатов расплавляемости стали с соответствующими расчетами на основе программного комплекса JMatPro подтвердил эффективность использования параметров межатомного взаимодействия в качестве модельних. Предлагаемые модели для определения расплавляемости хромоникелевых сталей рекомендованы к применению с содержанием основных элементов Cr, Ni от 0 до 30%. Результаты исследований рекомендуются к использованию в промышленных условиях посредством интеграции разработанных моделей в АСУТП сталеплавильного производства, что будет способствовать направленному формированию состава и свойств продуктов плавки, а также снижению энергетических затрат.

Ключевые слова: специальные стали, параметры межатомного взаимодействия, физико-химические свойства, микронеоднородность, прогнозные модели

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Роль врахування міжатомної взаємодії при прогнозуванні комплексу структурно-чуттєвих властивостей сталей та сплавів спеціального призначення

Метою роботи є виявлення впливу хімічного складу сталей і сплавів спеціального призначення на формування їх фізико-хімічних і структурно-чутливих властивостей. Це завдання вирішується шляхом математичного моделювання нероздільного ланцюжка «склад - структура - властивість» з урахуванням параметрів міжатомної взаємодії в розплаві на основі концепції спрямованої хімічного зв'язку. Розплав стали розглядається як хімічно однорідна система, а стан розплавів виражається через сукупність інтегральних параметрів, основними з яких є: Zy - параметр стану заряду системи (е); r - статистично середня меж'ядерна відстань (10^{-1}нм); tgα - постійна для кожного елемента, що характеризує зміну радіуса іона при зміні його заряду. На базі експериментальної інформації про властивості та з використанням параметрів міжатомної взаємодії запропоновано розрахункові моделі для прогнозування властивостей сталей і сплавів. У прогнозних моделях враховано параметри мікронеоднорідності сталі, що забезпечило високу точність оперативного прогнозу. Порівняльний аналіз отриманих результатів расплавляємості стали з відповідними розрахунками на основі програмного комплексу JMatPro підтвердив ефективність використання параметрів міжатомної взаємодії в якості модельних. Пропоновані моделі для визначення расплавляємості хромонікелевих сталей рекомендовано до застосування з вмістом основних елементів Cr, Ni від 0 до 30%. Результати досліджень рекомендуються до використання в промислових умовах за допомогою інтеграції розроблених моделей в АСУТП сталеплавильного виробництва, що сприятиме спрямованому формуванню складу і властивостей продуктів плавки, а також зниження енергетичних витрат.

Ключові слова: спеціальні стали, параметри міжатомної взаємодії, фізико-хімічні властивості, мікронеоднорідність, прогнозні моделі

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