INTRODUCTION

The radius of interaction between atoms of components in substitutional solid solutions corresponds approximately to ten or more coordination shells. It is explained by the electronic theory of alloys [1] and is testified experimentally by the method of diffuse scattering of X-rays and slow neutrons on crystals of alloys [2] and also by calculations of thermodynamic parameters in binary alloys [3]. It is paradoxical, but for binary solid solutions of carbon and nitrogen in gamma iron, we could use the model of pairwise interaction between interstitial atoms, in which the radius of interaction corresponds to only two nearest coordination shells formed by octahedral interstices in austenite. This model satisfactorily explains the experimental [4] intensities of Lorentz components of the Mössbauer spectra of iron in these alloys [4–6] as well as the thermodynamic properties of solid solutions of carbon in gamma iron [7].

In the modern metallurgy, multicomponent solid solutions containing both substitutional and interstitial impurities play an important part. One of such solutions is austenite, which contains, along with carbon, transition alloying elements. The authors of [8] used a model that assumes that the interaction of a carbon atom with an atom of a transition element in austenite takes place only if the latter atom occupies the site nearest to the octahedral interstice occupied by a carbon atom. This is the minimum-radius pairwise interaction model. In this model, the magnitude of the second-order thermodynamic cross-interaction parameter $\rho_{C,Ni}^C$ in the austenite at a temperature of 1273 K has been calculated. The results of the calculation ($\rho_{C,Ni}^C = 11.4$) satisfactorily agree with the experimental value ($\rho_{C,Ni}^C = 11.1$).

RESULTS AND DISCUSSION

This can be carried out using experimental thermodynamic data for low-alloy austenitic alloys of the Fe–C–Ni system. The three-particle C–Ni–C potential of approaching is taken equal to zero, i.e., basically we use the model of pairwise interaction.

For simplification, we designate the Fe, C, and Ni components of the solution by indices 1, 2, and 3, respectively. Let the carbon concentration be $c_2$ and the nickel concentration be $c_3$ (in mole fractions). The rational activity coefficients of carbon and nickel in the solution are designated as $\gamma_2$ and $\gamma_3$, respectively. Let the initial value of the carbon activity coefficient be $\gamma_2^0$, and the initial nickel activity coefficient, be $\gamma_3^0$. Using the principal thermodynamic expansion for low-concentration alloys [9], in the quadratic approximation in
the concentrations of dissolved components, we can write
\[
\ln \gamma_2 = \ln \gamma_3^1 + \varepsilon_2^{(2)} c_2 + \varepsilon_2^{(3)} c_3 + \rho_2^{(2)} c_2 \rho_2^{(3)} c_2 \varepsilon_2^{(3)} c_2,
\]
where \(\varepsilon_2^{(2)}\) and \(\varepsilon_2^{(3)}\) are the Wagner [10] interaction parameters; and \(\rho_2^{(2)}, \rho_2^{(3)}\) and \(\rho_2^{(2,3)}\) are the interaction parameters of the second order [9]. The parameter \(\rho_2^{(2,3)}\) is also called cross-interaction parameter. Let us calculate the magnitude of the \(\rho_2^{(2,3)}\) interaction parameter.

In an infinitely dilute nickel solution with small additions of carbon, the nickel activity is written, analogously to (1), as
\[
\ln \gamma_3 = \ln \gamma_3^0 + \varepsilon_3^{(2)} c_2 + \varepsilon_3^{(3)} c_3,
\]
where \(\varepsilon_3^{(2)}\) and \(\varepsilon_3^{(3)}\) are the interaction parameters of the first and the second order, respectively. The Gibbs–Duhem equation yields the following thermodynamic equations [9]:
\[
\varepsilon_3^{(2)} = \varepsilon_2^{(3)}
\]
and \(\rho_2^{(2,3)} + \varepsilon_3^{(3)} = 2\rho_3^{(2)} + \varepsilon_2^{(2)}\).

From here, it follows
\[
\rho_2^{(2,3)} = 2\rho_3^{(2)} + \varepsilon_2^{(2)} - \varepsilon_3^{(3)}.
\]

Consider an fcc lattice. We number the coordination shells of a site of this lattice by natural numbers in such a manner that the coordination shell with a larger radius corresponded to a larger order number, and each natural number corresponded to a unique coordination shell with a nonzero radius. Let \(z_i\) be the coordination number of the \(i\)th coordination shell of the lattice.

Consider the spatial lattice formed by octahedral interstices of the fcc lattice. This lattice by itself is an fcc lattice isomorphic to the lattice of sites. Let the \(i\)th coordination shell of the interstice lattice correspond to the \(i\)th coordination shell of the site lattice. Let \(z^*_i\) be the coordination number for the \(i\)th coordination shell of the interstice lattice. Then \(z^*_i = z_i\).

We number the neighborhoods of an octahedral interstice by the sites of the fcc lattice in accordance with the principles formulated above for the coordination shells of the lattice. Let \(\delta_j\) be the number of lattice sites in the \(j\)th neighborhood of the interstice. Let \(k^*_i\) be the number of sites of the fcc lattice at the intersection of the \(j\)th neighborhood of one octahedral interstice and \(k\)th neighborhood of another octahedral interstice located on the \(i\)th coordination shell of the first interstice.

The neighborhoods of a site of the fcc lattice by octahedral interstices will be numbered based on the isomorphism between the lattices of sites and interstices. Let \(k^*_{ijk}\) be the number of octahedral interstices at the intersection of the \(i\)th neighborhood of one lattice site and \(j\)th neighborhood of another site that is located on the \(i\)th coordination shell of the first one. Obviously, \(k^*_{ijk} = k_{ijk}\).

Let \(h^*_{ij}\) be the pair potential of interaction between carbon atoms in the austenite, where \(i\) is the order number of a coordination shell. Let \(h^*_{ij}\) be the pair potential for approach between nickel and carbon atoms, where \(j\) is the order number of the neighborhood of an octahedral interstice by lattice sites. Within the framework of the pairwise interaction model, the potential \(h^*_{ij}\) can be conventionally interpreted as follows:
\[
h^*_{ij} = u^*_{ij23} - u^*_{12},
\]
where \(u^*_{ij23}\) is the potential of interaction between carbon and nickel atoms, \(u^*_{12}\) is the potential of interaction between carbon and iron atoms.

Introduce quantities
\[
\varepsilon^*_{22} = 1 - \exp(-h^*_{ij}/k_B T)\]
and
\[
\varepsilon^*_{23} = 1 - \exp(-h^*_{ij}/k_B T),
\]
where \(k_B\) is the Boltzmann constant and \(T\) is the absolute temperature.

Let \(\beta\) be the number of octahedral interstices per one site in the lattice. According to the statistical theory [11], within the framework of the pairwise interaction model we have the following expressions for the thermodynamic parameters of interaction:
\[
\varepsilon_i^{(2)} = \frac{1 + \beta}{\beta} + \frac{1}{\beta} \sum_{i=1}^{\infty} z_i^* \varepsilon_i^{*22},
\]
\[
\varepsilon_i^{(3)} = \sum_{j=1}^{\infty} \delta_j \varepsilon_i^{*23},
\]
\[
\rho_i^{(2)} = -\frac{1 + \beta}{2\beta} + \frac{1}{2\beta} \sum_{i,j,k=1}^{\infty} z_i^* k_{ijk} \varepsilon_i^{*22} \varepsilon_j^{*23} \varepsilon_k^{*23} + \frac{1}{2\beta} \sum_{j=1}^{\infty} \delta_j \varepsilon_j^{*22} + \frac{1}{2\beta} \sum_{i=1}^{\infty} \delta_i \varepsilon_i^{*23} - \frac{1}{2\beta} \sum_{i,j=1}^{\infty} z_i^* \varepsilon_i^{*22}.
\]