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PHYSICAL AND CHEMICAL CONFORMITIES TO LAW FOR FORMING OF NONMETALLICS IN STEEL

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On the basis of Gibbs method for chemical potentials thermodynamics correlations are got, describing an origin and increase of nonmetallic in steel. Conformities to law of change of mass and chemical composition of nonmetallic in liquid steel at its cooling are certain. Methods over of determination of critical size of nonmetallic are brought. Possibility of formation of the heterogeneous including with a refractory kernel, saturated by the oxides of alkalite-earch metals, and fusible homogeneous shell is shown.
Keywords:

Raising of task. The problem to make thermodynamics description of nonmetallics in steel is in work, which will allow on composition of metal in number to estimate their mass, size and chemical composition set. On the first stage simplification according to which all endogenous liquid including have a spherical form is inputted. A non-metal phase, making nonmetallics, can have the different aggregate state and chemical composition; however existence of the most credible chemical composition of this phase, answering thermodynamics equilibrium in the system of «metal-NM» is assumed.

Basic part of researches. Curvature of surface of nonmetallics requires introduction to expression for chemical potential of every component in a non-metal phase composed λ, depending on a molar volume, radius of including and its specific superficial energy, named usually the amendment of Thomson-Gibbs [1]:

$$\lambda = \frac{2\sigma}{r} v^M \ , \qquad (1)$$

where σ - specific superficial energy (surface-tension); r - a radius of including; v^M - a molar volume.

Chemical potential of i component of nonmetallics will make:

$$\mu_{<i>} = \mu^0_{<i>} + R \cdot T \cdot \ln a_{<i>} + \lambda_i = \mu^0_{<i>} + R \cdot T \cdot \ln x_{<i>} \cdot \gamma_{<i>} + \lambda_i \ , \qquad (2)$$

where $\mu^0_{<i>}$ - chemical potential of clean component of i standard state; $a_{<i>}$ - activity of i component in a nonmetallics; $\gamma_{<i>}$ - a coefficient of activity of i component.

In the got expression the coefficients of activity of components it is expedient to calculate in accordance with the thermodynamics model of multicomponent liquid slag phase, taking into account valence of chemical elements [2]:

$$\ln \gamma_{<i>} = \ln \gamma'_{<i>} + \mu_{<e>} \cdot \nu_i = \nu_i \cdot \ln \psi_{<i>} + \sum_{j=1}^{k} x_{<j>} \cdot \nu_j \cdot \ 1 - \psi_{<j>} \cdot \beta_{<ji>} \ + \mu_{<e>} \cdot \nu_i \ , \gamma \qquad (3)$$

where $\gamma'_{<i>}$ - a coefficient of i component activity without the account of electrochemical element; $\mu_{<e>}$ - chemical potential of electrons (Fermi level); ν_i -

valence of i element; $\psi_{<i>} = \left(\sum_{j=1}^{k} x_{<j>} \cdot \beta_{<ij>} \right)^{-1}$; $\beta_{<ij>} = \exp\left(-\frac{\varepsilon_{<ij>}}{R \cdot T} \right)$; R - universal gas constant; T - an absolute temperature; $\varepsilon_{<ij>}$ - pair power parameters of co-operation.

The condition of thermodynamics equilibrium in the system of «metal-NM» is equality of chemical potentials of components (chemical elements) in a metal and nonmetallics.

At cooling of the system of constant of equilibrium of elements with positive valence increase, that results in appearance of non-metal phase. However, unlike a slag phase, the origin of nonmetallics depends also on their radius and corresponding sizes λi.

By the condition of coexistence in the system metallic and non-metal phases at a certain temperature there is equality of characteristic equation of $H = 0$ relatively $\mu_{<e>}$ at some set radius of including:

$$H = \sum_{i=1}^{k} n_i \cdot \left[1 - \exp\left(A_{<i>} - \lambda_i / R \cdot T - \mu_{<e>} \cdot \nu_i \right) \right] = 0 \ . \quad (4)$$

In default of decision of equation (4) it is possible to pick up such values λ_i, which a decision appears and a non-metal phase disappears. These values correspond to the critical radius of nonmetallics of r_c.

Change of Gibbs energy at the origin of nonmetallics it is possible to express as a function of his radius of r:

$$\Delta G_1 = -\frac{4\pi \cdot r^3}{3} \cdot \frac{\rho \cdot \sum_{i=1}^{k} x_{<i>} \cdot \Delta\mu'_{[i>}}{\sum_{i=1}^{k} x_{<i>} \cdot M_i} + 4\pi \cdot r^2 \cdot \sigma \ , \quad (5)$$

where $\Delta\mu'_{[i>}$ - a change of chemical potential of i component in its transition from a nonmetallics in a metal (without the amendment of Thomson-Gibbs).

If chemical potentials of elements less than, than in a metal ($\Delta\mu'_{[i>} > 0$) in a nonmetallics, motive force of transition of elements is created from a metal in including, and his height is possible.

Equating the first derivative G_1 on r to the zero, find a critical radius:

$$r_c = \frac{2\sigma}{\rho} \cdot \frac{\sum_{i=1}^{k} x_{<i>} \cdot M_i}{\sum_{i=1}^{k} x_{<i>} \cdot \Delta\mu'_{[i>}} \ . \quad (5)$$

As a non-metal phase, saturated CaO and MgO, in an initial period of increase of including has a high temperature of melting, formation of refractory kernel and subsequent layer increase with the gradient change of chemical composition from a center to the surface of hard phase is possible. If a non-metal phase at some relation of r/r_c becomes liquid from diminishing of content CaO and MgO, its chemical composition in future changes synchronously with the increase of radius, because equilibrium with a metal in the liquid nonmetallics of pony-size (< 1,0 mcm) is arrived at almost instantly. Thus including with difficult morphology - refractory kernel and fusible (or less refractory) homogeneous shell is formed.

Conclusions. The offered thermodynamics model of nonmetallics does not conflict with the before worked out model of multicomponent liquid slag phase, and fully coincides with its in default of curvature of interphase border and surface-tension.

REFERENCE

1. **Люпис, К.** Химическая термодинамика материалов [Текст] / К. Люпис. – М. : Металлургия, 1989. – 503 с. – ISBN 5-229-00001-5.
2. **Харченко, А. В.** Термодинамическая модель многокомпонентной жидкой шлаковой фазы / А. В. Харченко, Р. В. Синяков // Металургія : наукові праці Запорізької державної інженерної академії. – Запоріжжя : РВВ, 2016. – Вип. 2(36). – С. 16-22.