

Simulation of the α - $\beta(\alpha')$ phase equilibrium of metal hydrides within the perturbation theory

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A model of non-ideal (interacting) lattice gas is used to study phase equilibria in metal hydrides within the thermodynamic perturbation theory. The calculated decomposition curves of PdH_x and NbH_x disordered phases and temperature dependences of pressure within the isotherm plateau of hydrogen solubility match well with experimental data. Mathematical expressions have been obtained for decomposition enthalpy and entropy of hydride phases and PCT-dependences (both below and above the α - β transition critical point). CT and PCT diagrams have been drawn for different versions of the proposed model.

Модель неидеального (взаимодействующего) решеточного газа применена для исследования фазовых равновесий в металлгидридах методом термодинамической теории возмущений. Рассчитанные кривые распада неупорядоченных фаз гидридов PdH_x , NbH_x и температурные зависимости давления на плато изотерм растворимости водорода хорошо согласуются с экспериментальными данными. Получены выражения для энтальпии и энтропии разложения гидридных фаз и для PCT-зависимостей как ниже, так и выше критической точки α - β -перехода. Построены CT- и PCT-диаграммы в различных вариантах предложенной модели.

In the preceding works [1, 2], we have described thermodynamically the hydrogenic subsystem of transition metal hydrides (MH) basing on the proposed model of non-ideal (interacting) lattice gas of H atoms taking into account both the direct (H-H) interaction and the metal matrix expansion under hydrogen dissolution. The lattice gas equilibrium properties have been determined using the modified perturbation theory (MPT) for the basis case of inclusion solutions with the only type of equivalent interstices. This allowed to draw some conclusions concerning origin of observed features of MH phase diagrams in the region of disordered α - $\beta(\alpha')$ phases (asymmetry of decomposition curves, positions of critical points, etc.).

Within the model mentioned, a relationship has been established between the macroscale characteristics of Me-H solutions, in particular, the phase transition pa-

rameters [2], and microscopic (atomic) characteristics of the hydrogen subsystem and the metal lattice. The initial crystal structure of the individual metal is assumed to be identical with the Me sublattice of the MeH_x hydride. Since the metal atomic packing remains unchanged at the mentioned $\alpha \rightarrow \beta(\alpha')$ transition types, the chemical potential $\mu_{\text{H}} = G_{\text{H}}/N_{\text{H}}$ of the H component of a MH, that is, the specific Gibbs energy per H atom, G_{H} , has the form

$$\beta\mu_{\text{H}}^{\dagger}(\theta, T) = \ln \frac{\theta}{1-\theta} + \frac{W_1\theta}{T(1+\alpha c_s\theta)} + \frac{W_2\theta^2}{T^2(1+\alpha c_s\theta)^2}, \quad (1)$$

where $\beta = 1/kT$, $\mu_{\text{H}}^{\dagger} = \mu_{\text{H}} - \mu_{\text{H}}^{\text{St}}$; $\mu_{\text{H}}^{\text{St}}(T)$ chemical potential in the standard state