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THERMODYNAMICS OF HETEROGENEOUS CATALYSIS PROCESSES

THE INFLUENCE OF MICRODISTORTIONS OF THE CRYSTAL LATTICE OF A SOLID

In work ([1]), a thermodynamic method was proposed for investigating irreversible processes of heterogeneous catalysis. For the case of a surface reaction of recombination of gas atoms, on the basis of the Gibbs equations and the law of conservation of energy for two phases, the basic equations characterizing the kinetics of the catalytic process were obtained. In accordance with the concepts developed, the internal thermodynamic forces of the solid phase—elastic stresses, the stress of work hardening, magnetization, etc.—may exert a substantial influence on the kinetics of the process. At the same time, it is necessary to determine whether the indicated parameters are a driving force of the catalysis process (the case of intersecting thermodynamic fluxes) or only contribute to the processes of energy exchange and its dissipation in the solid.

In the present work, the role of relative microdistortions of the crystal lattice (stresses of the second kind) of a metal in the thermodynamics of heterogeneous catalysis is investigated. As a model, the reaction of recombination of hydrogen atoms on the surface of work-hardened and recrystallized molybdenum specimens was used at temperatures below the onset of recovery and recrystallization processes.

As is known, strengthening (work hardening) of a material occurs under inelastic deformation of a body and is accompanied by the transition of part of the mechanical work into latent energy of deformation, which is converted into heat during recrystallization annealing of the specimen.

Each form of internal energy of a thermodynamic system corresponds to two conjugate parameters. In the case of work hardening they may be called the stress of hardening (a generalized force) and simply hardening. On the basis of Curie' s theorem, stating that in an isotropic medium forces of one tensorial order cannot produce fluxes of another tensorial order, it was shown in work (^{2}) that these parameters are tensors of the second rank in three-dimensional space. Let us denote them, respectively, by z_{ij} and h_{ij} $(i, j = 1, 2, 3)$.

Then the production of entropy in an open two-phase system takes the form:

$$\sigma = \left(\frac{1}{T_2} - \frac{1}{T_1}\right) qS + \frac{1}{T_1} A \left(\xi + \sum_{\gamma=1}^{r} \dot{n}_{\gamma e} \Big/ \sum_{\gamma=1}^{r} \nu_\gamma \right) - \frac{1}{T_1} \sum_{\gamma=1}^{r} \mu_\gamma \dot{n}_{\gamma e} - \frac{1}{T_2} \sum_{i,j=1}^{3} z_{ij} \dot{h}_{ij}, \qquad (1)$$

where the same notation is used as in work (^{1}). Since q, ξ, $n_{\gamma e}$ are scalars, whereas z_{ij} is a tensor of the second rank, the linear dependences between fluxes and forces, in accordance with Curie' s theorem, will be

$$qS = L_{11}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + L_{12}\frac{A}{T_1};$$

$$\xi + \sum_{\gamma=1}^{r} \dot{n}_{\gamma e} \Big/ \sum_{\gamma=1}^{r} \nu_\gamma = L_{12}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + L_{22}\frac{A}{T_1}; \qquad (2)$$

$$-\dot{n}_{\gamma e} = \sum_{\beta=1}^{r} P_{\gamma\beta}\frac{x_\beta}{T_1} \quad (\gamma = 1, \dots, r);$$

$$-\dot{h}_{ij} = \sum_{\alpha,\beta=1}^{3} R_{ij\alpha\beta} z_{ij} \quad (i, j = 1, 2, 3), \qquad (2)$$

i.e., $\dot{h}_{ij}$ does not cross-couple with the other fluxes. At the same time, the coefficients $L_{11}, L_{12}, L_{22}, P_{\gamma\beta}, R_{ij\alpha\beta}$ are functions of the thermodynamic parameters of the system, in particular of the hardening h_{ij}. In this case the heat capacity c_2 of the solid phase also depends on h_{ij}.

It follows from the analysis carried out that microdistortions of the crystal lattice of a metal cannot be the driving forces of catalysis. Their role in the given process is manifested, above all, in the dependence of L_{11}, L_{12} on h_{ij}, which may be represented physically as a certain increase in the effective surface area of the specimen upon work hardening (a larger number of active reaction sites). The latter, as is known, promotes intensification of the catalytic process (an increase in L_{12}). On the other hand, the presence in the metal of latent deformation energy leads to a decrease in the heat capacity c_2, and at temperatures close to the recrystallization temperature it may lead to a certain slowing of the reaction as a result of the conversion of the latent deformation energy into heat.

Fig. 1. Temperature dependence of the number of hydrogen atoms recombining on the surface of molybdenum wire: 1—recrystallized, 2—work-hardened.

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In the experiment studying the influence of metal hardening on the kinetics of recombination of hydrogen atoms, the quantities of relative microdistortions $\varepsilon_1, \varepsilon_2$, arising during drawing of molybdenum wire, were used as the criterion of hardening. These quantities are components of the tensor h_{ij} in the directions along and across the drawing axis. The determination of $\varepsilon_1, \varepsilon_2$ was carried out by the method of harmonic analysis of the intensity curve of the diffraction line ([3]). To find the latter from the angular width of the diffraction line, an x-ray unit with ion registration was used (URS-50I).

Despite the fact that line broadening, which is an x-ray diffraction indication of microdistortions, may also be caused by another reason—the fine dispersion of the specimen—nevertheless, from the shape of the broadened line it is possible ([4]) to establish the cause of its broadening and to give a quantitative estimate of the effect that caused this broadening. It is sufficient to expand in a Fourier series the intensity curve of the broadened line and the intensity curve of a line whose width depends only on the geometrical conditions of recording, and to take the ratio of the corresponding expansion coefficients in order to obtain the coefficients A_t of the Fourier expansion of the curve of true broadening. When the grain sizes are large, the coefficients A_t give a complete characterization of the degree of distortion of the crystal lattice.

Recrystallization of the specimens was carried out by annealing them after drawing in a high-frequency vacuum furnace for 2 h at 1200°. For the work-hardened specimen, the obtained intensity profiles of the diffraction lines from the reflection planes (110) and (200)—the most intense lines for the crystal lattice of molybdenum—were processed.

As a result of the calculation, the following values of the relative microdistortions (work hardening) were obtained: $\varepsilon_1 = h_{11} = 1.947 \cdot 10^{-3}$; $\varepsilon_2 = h_{22} = h_{33} = 1.329 \cdot 10^{-3}$.

In order to determine the nature of the influence of the degree of distortion of the crystal lattice of a solid on its catalytic activity, experiments were carried out on the recombination of hydrogen atoms (pressure $P_H = 0.047$ mm Hg) on the surface of recrystallized ($h_{11} = h_{22} = h_{33} = 0$) and work-hardened ($h_{11} = 1.947 \cdot 10^{-3}$, $h_{22} = h_{33} = 1.329 \cdot 10^{-3}$) molybdenum. The method of investigation was analogous to (5).

The temperature range of the investigations in the case of work-hardened specimens was 200—400° and was appreciably lower than the temperatures at which

Fig. 2. Temperature dependence of the recombination coefficients of H atoms on the surface of molybdenum: 1—recrystallized, 2—work-hardened

Figure 2: Fig. 2. Temperature dependence of the recombination coefficients of H atoms on the surface of molybdenum: 1—recrystallized, 2—work-hardened

recrystallization begins. As shown by the X-ray diffraction patterns taken by us from specimens of stretched molybdenum wire annealed at various temperatures (the exposures were made in a small Debye camera RKD-57.3 with copper radiation), the effect of broadening of the diffraction lines disappears only in X-ray diffraction patterns of specimens annealed at 600—700° (distinct splitting of the doublet).

Fig. 2. Temperature dependence of the recombination coefficients of H atoms on the surface of molybdenum: **1**—recrystallized, **2**—work-hardened

The curves obtained in the experiment, characterizing the rate of the recombination process of atoms, are presented in Fig. 1. In Fig. 2 the temperature dependence of the recombination coefficients $\gamma_{\mathrm{H/Mo}}$ is given, from which the mean values of the apparent activation energy E of the surface reaction are calculated graphically. For the work-hardened and non-work-hardened states of the crystal lattice of molybdenum they are equal, respectively, to 2650 and 2160 cal/g-mole. The obtained value $\Delta E = 490$ cal/g-mole apparently represents the total energy of residual distortions—the latent deformation energy for this work hardening (6). The presence of a higher energy barrier for the recombination of atoms in the case of the work-hardened metal is associated with a certain decrease, upon work hardening, in the characteristic temperature and a corresponding decrease in the heat capacity.

The mean value of the constant L^*_{12} of the rate of heterogeneous recombination of hydrogen atoms on work-hardened molybdenum, calculated according to (1), is $1.39 \cdot 10^{-5}$ mole/cm^2·sec (mean error of determination 6.13%) and exceeds by a factor of 1.65 the value of L^*_{12} for the case of using recrystallized molybdenum wire as the catalyst.

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