HOW THE POLARITY OF A SURFACE REACTING WITH A LOW-TEMPERATURE PLASMA AFFECTS THE THERMODYNAMIC VARIABLES IN METALLURGICAL REACTIONS[1])

V. DEMBOVSKÝ[2]), Ostrava

Reactionships are presented for calculating the changes in thermodynamic variables which attend heterogeneous metallurgical reactions involving a low-temperature plasma, on the assumption that this plasma is in thermodynamic equilibrium state and that its composition is known. A positive polarity of the reacting surface is shown to reduce the thermodynamic probability of the desired reaction taking place. A negatively charged reacting surface allows metals to be gained by the hydrogen reduction of even extremely stable oxides. As the following expressions neglect the recombination processes in the thermal boundary layer, the equations derived for the particle flow densities at the reacting surface are not absolutely accurate. They are, however, accurate enough for all practical purposes.

КАКОЕ ВЛИЯНИЕ ОКАЗЫВАЕТ ПОЛЯРНОСТЬ ПОВЕРХНОСТИ, РЕАГИРУЮЩЕЙ С НИЗКОТЕМПЕРАТУРНОЙ ПЛАЗМОЙ, НА ТЕРМОДИНАМИЧЕСКИЕ ПЕРЕМЕННЫЕ В МЕТАЛЛУРГИЧЕСКИХ РЕАКЦИЯХ

В работе приведены соотношения для расчета изменений термодинамических переменных, которые сопровождают гетерогенные металлургические реакции с низкотемпературной плазмой, в предположении, что плазма находится в термодинамическом равновесном состоянии и что ее состав известен. Показано, что положительная полярность реагирующей поверхности уменьшает тер-модинамическую вероятность происхождения данной реакции. Отрицательно заряженная поверхность допускает, чтобы металлы приобретали при помощи восстановления водородом даже особо устойчивые окиси. Поскольку данные выражения пренебрегают процессами рекомбинации в термическом граничном слое, уравнения, выведенные для плотностей потока частиц на реагирующей поверхности, не являются абсолютно точными. Их точность, однако, достаточна для всех практических целей.

I. PHYSICAL INTERACTIONS OF ACTIVE PARTICLES IN THE ABSENCE OF AN EXTERNALLY APPLIED ELECTRIC FIELD

The basic metallurgical reactions exploited for extractive and refining processes take place predominantly in heterogeneous systems. In a heterogeneous system incorporating a plasma, the component in the plasma state is generally the extracting or refining medium, while the processed material is in the solid or liquid state.

The density of the flow of active particles of the jth kind, reaching an electrically insulated surface that is in contact with the plasma stream, is given by a generalized expression

$$\psi_j = \frac{n_j v_{s,j}}{4} \qquad (1)$$

where n_j is the concentration of particles of this jth kind in the surrounding plasma stream, $v_{s,j}$ is the arithmetic mean velocity of the jth kind.

After substituting the numerical values of the constants in the formula describing the arithmetic mean velocity of the particles,

$$v_{s,j} = \left(\frac{8kT_j}{\pi m_j}\right)^{1/2} = 5.93 \times 10^{-12}\left(\frac{T_j}{m_j}\right)^{1/2} \qquad (2)$$

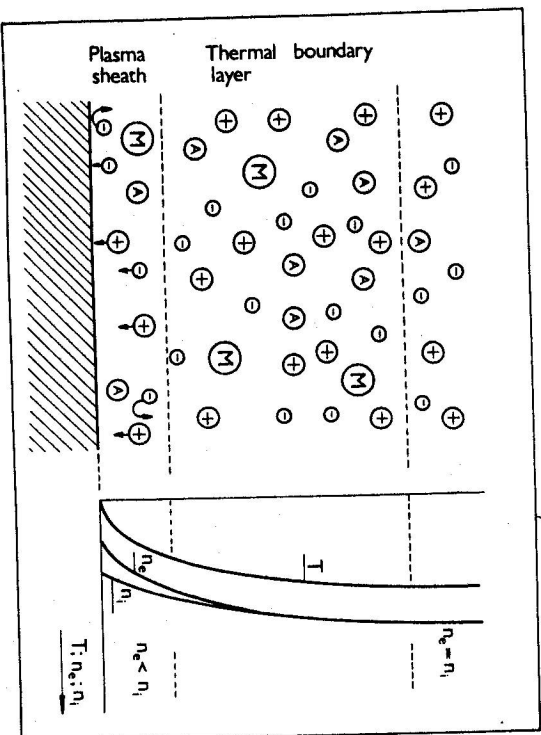where k is the Boltzmann constant (1.38054×10^{-23} JK^{-1}), T_j is the ther-

Fig. 1. Scheme of the transport of active particles from a lowtemperature plasma to the reacting surface in the absence of an applied electric field.

modynamic temperature of particles of the jth kind, and m_j is the mass of particles of the j-th kind, and inserting the resultant expression into equation (1), we obtain a formula better suited for routine calculations:

$$\psi_j = 1.48 \times 10^{-12}\, n_j \left(\frac{T_j}{m_j}\right)^{1/2} \qquad [\text{m}^{-2}\,\text{s}^{-1}] \qquad (3)$$

A scheme of a heterogeneous system in the absence of an externally applied electric field, showing the transport of active particles from the plasma to the surface of the processed material, is presented in Fig. 1.

II. HETEROGENEOUS SYSTEMS IN THE PRESENCE OF AN APPLIED ELECTRIC FIELD

When the electrically conductive charged surface is incorporated in the plasma torch circuit, or when a voltage is applied across this surface and the plasma stream, the situation arising conforms essentially to the scheme in Figs. 2 or 3, depending on the polarity of the charged surface.

When the surface charge is negative in polarity, the ions that impinge on it deliver a current density J_i, which varies with the voltage drop across the collision-free plasma sheat and with the thickness of that sheath [1], as follows:

$$J_i = \frac{1}{9\pi}\left(\frac{2e}{m_i}\right)^{1/2}\frac{V_s^{3/2}}{d_s^2}\left[1 + 2.66\left(\frac{kT_i}{eV_s}\right)^{1/2}\right] \qquad [\text{Am}^{-2}] \qquad (4)$$

where d_s is the thickness of the plasma sheath [m], m_i is the mass of an ion [kg], e is the charge of an electron (1.60210×10^{-19} C), T_i is the thermodynamic temperature of the ions, and V_s is the voltage drop across the sheath, i.e. within d_s, which in this case corresponds to the anode voltage gradient [V] and is defined as [2]

$$V_s = \frac{1}{2}\frac{kT_e}{e}\ln\left(\frac{2m_i}{\pi m_e}\right). \qquad (5)$$

When the surface is negatively charged, the density of the flow of singly ionized positive ions impacting on it is given by

$$\psi_i = \frac{J_i}{e}. \qquad (6)$$

In a heterogeneous system where the conductive charged surface forms the cathode the density of the flow of singly ionized ions reaching that solid or liquid surface from the plasma can be established from the relation

$$\psi_i = \frac{I}{F_\kappa e} - \frac{J_i}{e} \qquad (7)$$

where I is the discharge current [A], and F_k the active area of the cathode or cathode spot [m²].

III. COMPARISON OF THE THERMODYNAMIC PARAMETERS OF REACTIONS INVOLVING A LOW-TEMPERATURE PLASMA

Let us assume that in a reaction described by

$$B + D_2 \rightarrow C + R \tag{8}$$

the diatomic molecules of substance D_2 enter reaction (8) in the form of a low-temperature plasma made up of molecules, atoms, ions and electrons. This reaction will then be described by

$$B + xD_2 + 2yD + 2zD^+ + 2ze \rightarrow C + R \tag{9}$$

where x, y and z are the molar fractions of particles on the molecular, atomic and ionic states, respectively. If in the course of this reaction the atoms and ions of substance D recombine, then the standard heat of the metallurgical reaction for the process conforming to scheme (9) will be

$$\Delta H^0 = [\Delta H_C^0 + \Delta H_R^0] - \{\Delta H_B^0 + x\Delta H_{D_2}^0 + 2y\frac{1}{2}(\Delta H_{dis}^0)_{D_2} + 2z[\frac{1}{2}(\Delta H_{dis}^0)_{D_2} + (\Delta H_{ion}^0)_D]\}. \tag{10}$$

The change in standard entropy will be determined by

$$\Delta S^0 = [S_C^0 + S_R^0] - \{S_B^0 + xS_{D_2}^0 + 2y\frac{1}{2}[S_{D_2}^0 + (\Delta S_{dis}^0)_{D_2}] + 2z[\frac{1}{2}S_{D_2}^0 + \frac{1}{2}(\Delta S_{dis}^0)_{D_2} + (\Delta S_{ion}^0)_D]\}. \tag{11}$$

The change in the standard Helmholtz energy can be ascertained from

$$\Delta F^0 = [\Delta F_C^0 + \Delta F_R^0] - \{\Delta F_B^0 + x\Delta F_{D_2}^0 + 2y\frac{1}{2}(\Delta F_{dis}^0)_{D_2} + 2z[\frac{1}{2}(\Delta F_{dis}^0)_{D_2} + (\Delta F_{ion}^0)_D]\}. \tag{12}$$

The change in the standard Gibbs energy caused by the metallurgical reaction will be

$$\Delta G^0 = [\Delta G_C^0 + \Delta G_R^0] - \{\Delta G_B^0 + x\Delta G_{D_2}^0 + 2y\frac{1}{2}(\Delta G_{dis}^0)_{D_2} + 2z[\frac{1}{2}(\Delta G_{dis}^0)_{D_2} + (\Delta G_{ion}^0)_D]\}. \tag{13}$$
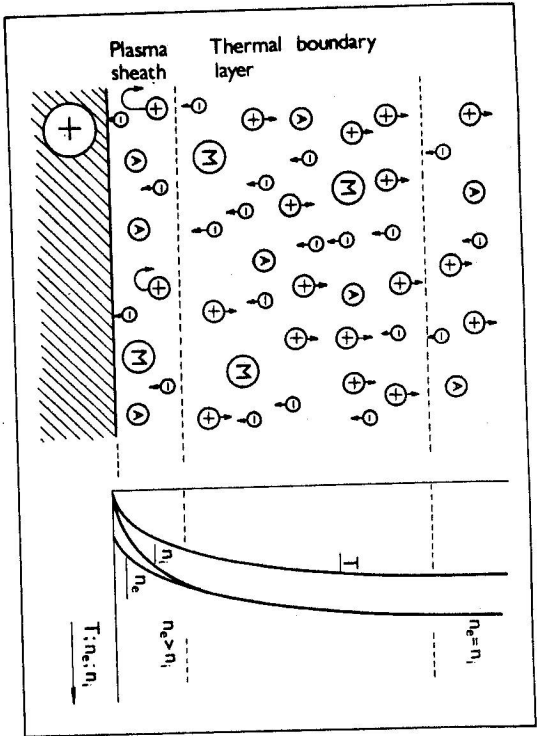

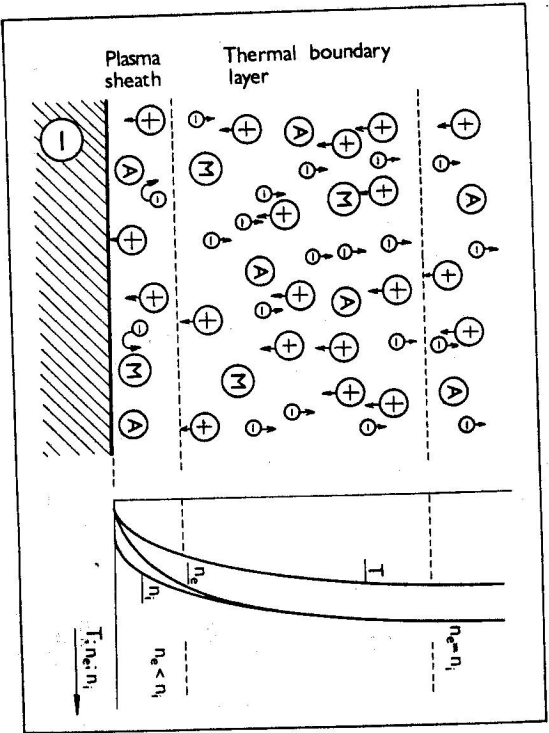Fig. 2. Scheme of the transport of active particles from a low-temperature plasma to a positively charged reacting surface.

Fig. 3. Scheme of the transport of active particles from a low-temperature plasma to a negatively charged reacting surface.

where

$$+ 2z\left[\frac{1}{2}\left((\Delta G^0_{dis})_{D_2} + (\Delta G^0_{ion})_D\right)\right]\}$$

n_{D_2}, n_D and n_{D^+} being the concentrations of molecules, atoms and ions, respectively, of substance D which participe in this reaction. The general definition of the size of any molar fraction is

$$x = \frac{n_{D_2}}{n_{D_2} + n_D + n_{D^+}}; \quad y = \frac{n_D}{n_{D_2} + n_D + n_{D^+}}; \quad z = \frac{n_{D^+}}{n_{D_2} + n_D + n_{D^+}}$$

$$x, y, z = \frac{n_i}{\sum n_i} \tag{14}$$

where n_i is the concentration (particle number density) of particles of the jth kind that participate in the reaction. When we deal with plasma processes, however, the molar fraction of the various particle kinds which constitute the plasma are far better expressed in terms of the particle flow densities on the reacting surface. Equation (1) shows that the density of a particle flow is directly proportional to the product of two variables: the concentration of those particles, n_i, and their arithmetic mean velocity, $v_{s,i}$. Upon inserting the expanded expression for the particle concentration obtained from formula (1),

$$n_i = 4\psi_i \left(\frac{\pi m_i}{8kT_i}\right)^{1/2} \tag{15}$$

into formula (14), we can set up an equation for calculating the molar fractions of various kinds of reacting particles in terms of the particle flow densities:

$$x, y, z = \frac{\psi_i (m_i)^{1/2}}{\sum \psi_i (m_i)^{1/2}} \tag{16}$$

where $\sum \psi_i$ is the total density of all the reacting particle flows on the surface with which they react. For the reaction described by scheme (9) we can thus formulate the molar fractions of the various reacting particle kinds as follows:

$$x = \frac{\psi_{D_2}(m_{D_2})^{1/2}}{\psi_{D_2}(m_{D_2})^{1/2} + \psi_D(m_D)^{1/2} + \psi_{D^+}(m_{D^+})^{1/2}}$$

$$y = \frac{\psi_D(m_D)^{1/2}}{\psi_{D_2}(m_{D_2})^{1/2} + \psi_D(m_D)^{1/2} + \psi_{D^+}(m_{D^+})^{1/2}}$$

$$z = \frac{\psi_{D^+}(m_{D^+})^{1/2}}{\psi_{D_2}(m_{D_2})^{1/2} + \psi_D(m_D)^{1/2} + \psi_{D^+}(m_{D^+})^{1/2}}. \tag{17}$$

In practice most metallurgical reactions take place at roughly constant pressures and temperatures. Under such conditions their termodynamic probability is

governed by the attendant changes in the Gibbs energy: a metallurgical reaction will proceed by the more completely and perfectly, the more negative the value of the change is, e.e. the greater the decrement in the Gibbs energy. The course of these changes, in dependence on the temperature of the reacting system, can be computed by the conventional procedure with the aid of the Gibbs—Helmholtz equations.
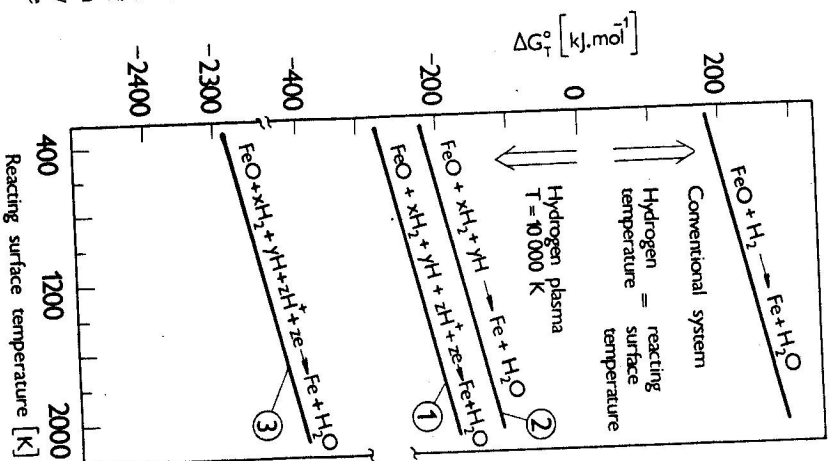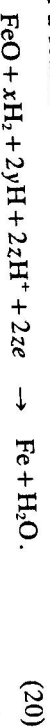
Fig. 4. How the changes in the Gibbs energy attending the reduction of FeO by a hydrogen plasma at 10 000 K vary with the temperature of the reacting surface: 1 — in the absence of an applied electric field; 2 — with a positive polarity of the surface; 3 — with a negative polarity of the surface.

ΔG^0_T [kJ.mol⁻¹]

200 — 0 — −200 — −400 — −2300 — −2400

$FeO + H_2 \rightarrow Fe + H_2O$ — Conventional system

Hydrogen temperature = reacting surface temperature

Hydrogen plasma T = 10 000 K

$FeO + xH_2 + yH + zH^+ + ze \rightarrow Fe + H_2O$ ①

$FeO + xH_2 + yH + zH^+ + ze \rightarrow Fe + H_2O$ ②

$FeO + xH_2 + yH + zH^+ + ze \rightarrow Fe + H_2O$ ③

Reacting surface temperature [K]: 400 — 1200 — 2000

Fig. 4 shows the changes in the Gibbs energy at various temperatures of the reacting surface of solid iron oxide when the latter is reduced by a hydrogen plasma at 10 000 K, in a reaction described by

$$FeO + xH_2 + 2yH + 2zH^+ + 2ze \rightarrow Fe + H_2O. \tag{20}$$

The changes in the Gibbs energy, ascertained by the techniques outlined in this paper, show that a positive polarity of the reacting surface reduces the ther-

modynamic polarity of this reaction, as against the state when no external electric field was applied. In the extreme case of a fully ionized hydrogen plasma, Fig. 2 indicates that a situation may arise where no hydrogen particles will participate in interactions with the FeO surface, so that no reaction will take place. This probability increment suggests that, given a negatively charged reacting surface, reduction with a hydrogen plasma will permit metals to be gained even from highly stable oxides.

REFERENCES

[1] Cobine, J. D.: Gaseous Conductors. Dower, New York 1958.
[2] Thompson, W. D.: An Introduction to Plasma Physics. Pergamon Press, Oxford 1962.