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THE PROBLEM OF DIVERSE TEMPERATURES IN METALLURGICAL REACTIONS INVOLVING A THERMAL PLASMA1)

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When metallurgical reactions are carried out in heterogeneous systems which include a plasma, the plasma temperature substantially exceeds the temperature of the solid or liquid surface of the charge material. Under such circumstances the thermal plasma retains its thermic equilibrium and Maxwellian energy distribution only when it is interacting with a surface from which the floating electric potential is abstracted as it forms. In all other cases, i.e. if the surface is electrically insulated or if it forms the anode or cathode of the plasma-generating arc discharge circuit, the energy distribution differs from the Maxwellian model, and the effective or r.m.s. translational temperatures of the electrons, ions, and electrically neutral particles differ from each other.

I. INTRODUCTION

When either extractive or refining metallurgical processes are carried out by means of a plasma, the fundamental metallurgical reactions generally take place in a heterogeneous system: the extractive or refining agents are as a rule in the plasma state, while the raw materials or treated metals are in the solid or liquid state. The plasma used for metallurgical processing is usually gained by an arc discharge.

Plasma torches which employ a non-transferable or a superimposed arc may be utilized when the reacting solid or liquid surface is electrically insulated or when its electric potential is abstracted in the course of the process. However, in the more prevalent techniques the solid or liquid charge material is electrically incorporated in the arc discharge circuit.

The great majority of present-day plasma metallurgy processes are conducted at or near atmospheric pressure, or about 10^5 Pa. Under these conditions the plasma taking part in reactions in a heterogeneous system is a thermal plasma,

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i.e., a plasma in a state of thermic equilibrium; that means the temperatures related to the translational motions of the particles are described by $T_e = T_i = T_0 = T_{pl}$: the electron, ion, and neutral particle temperatures are all equal to the plasma temperature. In a thermal plasma, the particle velocity distribution and kinetic energy distribution are Maxwellian; the number density of the excited particles follows a Boltzmann distribution; and the number densities of electrons, ions, and electrically neutral particles are described by the Saha equation [1].

The thermodynamic calculations used to determine the equilibrium states and kinetics of conventional metallurgical reactions are based on the assumption of a Maxwellian distribution of particle velocities and energies in the reacting systems; and this distribution implicitly postulates one single system temperature. Therefore, the temperature conditions in an unconventional heterogeneous system that incorporates a thermal plasma have been analysed with the aim of establishing schemes which would allow thermodynamic investigations of the physical and chemical reactions proceeding at the solid or liquid surface of the material that is being treated.

II. TEMPERATURE GRADIENT DISTRIBUTION AT THE SURFACE, AND TEMPERATURE DISTRIBUTION IN THE PLASMA SHEATH

In the zone where the plasma contacts the much cooler solid or liquid surface, the resultant temperature gradient is concentrated in a thermal boundary layer. This layer is where recombination and relaxation processes take place. The electrically neutral particles, ions and electrons from the surrounding plasma cross this layer, to reach the reacting surface, by diffusion mechanisms. Fig. 1 is a scheme of the distribution of electron, ion, and neutral particle temperatures in the proximity of the reacting surface, assuming the absence of any electric field.

It follows from statistical thermodynamics that

$$\frac{\vartheta_e}{\vartheta_i} = \left(\frac{m_i}{m_e}\right)^{1/2}, \tag{1}$$

where ϑ_e and ϑ_i are the arithmetic mean velocities of the thermal motions of electrons and ions, and m_e and m_i are the masses of electrons and ions, respectively.

Equation (1) implies that ϑ_e is much greater than ϑ_i, and hence that the flow of electrons impinging on the surface will initially be much greater than the ion flow. If the surface is electrically insulated, this greater electron flow will persist until the negative charge built up on the surface becomes sufficient to repel further electrons. This leads to the formation of different potentials between the plasma and the surface. A further thin layer arises within the thermal boundary layer, close to the surface; this is known as the plasma sheath, d_s, with a thickness comparable with the size of the Debye radius. The floating electrical potential at the surface is given by the equation [2]

$$\varphi_s = \frac{k\,T'_e}{2e} \ln \frac{T'_e}{T'_i}\,\frac{m_i}{m_e} \tag{2}$$

where k is the Boltzmann constant, e — the electron charge, and T'_e and T'_i are the electron and ion temperatures, respectively, at the outer surface of the plasma sheath.

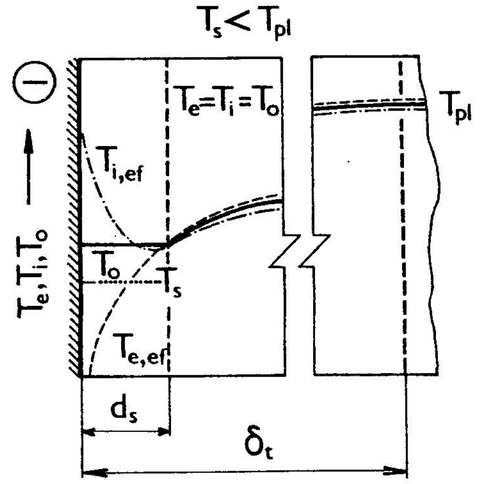

Fig. 1. Distribution of the translational temperatures of electrons, ions and electrically neutral particles at a surface cooler than the thermal plasma, when the floating potential is abstracted; this case is typical for plasma techniques where the charge material is not incorporated in the plasma torch circuit and is, for the sake of safety, grounded/earthed. T_s, T_{pl} — charge surface and thermal plasma temperatures, respectively; T_e, T_i, T_0 — translational temperatures of electrons, ions, and electrically neutral particles, respectively; $T_{e,ef}$, $T_{i,ef}$, $T_{0,ef}$ — effective or r.m.s. translational temperatures of electrons, ions, and neutral particles, respectively; δ_t — thermal boundary layer; $\bar{l}$ — collision-free path length.

The thermal effects of the drift energy of the particles, as the latter approach the solid or liquid surface, are comparable in magnitude with the similar effects of the energy of chaotic or random particle motions. For the most probable kinetic energy of particles with one degree of freedom, the way the drift of electrons and ions across the collision-free zone increases these thermal effects can be defined as follows:

For electrons: $$\varphi_s e = 1/2\, m_e v_e^2 = 1/3\, k\, \Delta T'_e, \tag{3}$$

For ions: $$-\varphi_s e = 1/2\, m_i v_i^2 = 1/3\, k\, \Delta T'_i, \tag{4}$$

where v_e and v_i are the most probable drift velocities of electrons and of ions, respectively.

For three degrees of freedom, the corresponding decrease in the translational temperature of electrons and the increment in the translational temperature of ions works out as

$$\Delta T'_e = 3\, \frac{\varphi_s e}{k} \tag{5}$$

$$\Delta T'_i = 3\, -\frac{\varphi_s e}{k}. \tag{6}$$

The electrons which under the action of the floating potential pass from the thermal boundary layer across the plasma sheath have an energy consisting of two components: the energy of chaotic motions, and the drift energy:

$$E_e = 1/2\, m_e \vartheta_e^2 - 1/2\, m_e v_e^2 \tag{7a}$$

while at the same time

$$E_e = k(T'_e - \Delta T'_e) = k\, T_{e,\, ef}. \tag{7b}$$

Similarly, the energy of the ions is

$$E_i = 1/2\, m_i \vartheta_i^2 + 1/2\, m_i v_i^2 \tag{8a}$$

while at the same time

$$E_i = k(T'_i + \Delta T'_i) = k\, T_{i,\, ef} \tag{8b}$$

and the energy of the electrically neutral particles is

$$E_n = 1/2\, m_0 \vartheta_0^2 = k\, T'_0 = k\, T_{0,\, ef}, \tag{9}$$

where $T_{e,\, ef}$, $T_{i,\, ef}$ and $T_{0,\, ef}$ are the effective or r.m.s. translational temperatures of the electrons, ions, and neutral particles, respectively, approaching the surface.

The negative potential created on the surface by the preferential impingement of electrons increases the r.m.s. (root mean.square) translational temperature of the ions while reducing that of the electrons. The r.m.s. translational temperature of electrons is by definition

$$T_{e,\, ef} = T'_e + \Delta T'_e \tag{10}$$

and that of ions is

$$T_{i,\, ef} = T'_i + \Delta T'_i. \tag{11}$$

Equations (9) to (11) indicate that

$$T_{e,\, ef} < T_{0,\, ef} < T_{i,\, ef}. \tag{12}$$

Fig. 2 presents a scheme of the distribution of the r.m.s. translational temperatures of neutral particles, electrons and ions as the particles pass from the thermal plasma to an insulated, electrically conductive surface.

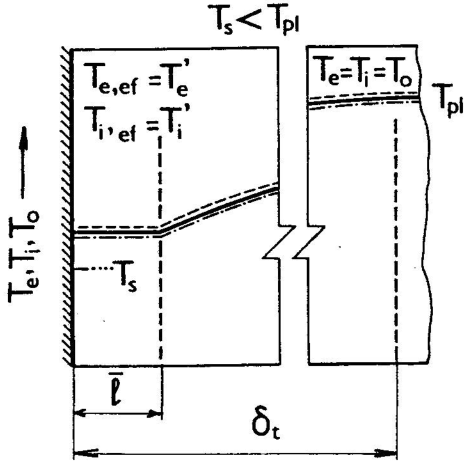

Fig. 2. Distribution of effective or r.m.s. translational temperatures of particles approaching an electrically insulated but conductive surface; this scheme is typical for fluid-layer plasma technologies, where pulverous powdery materials are introduced into a plasma stream, d_s — plasma sheath; otherwise notation as in Fig. 1.

III. PARTICLE TEMPERATURE DISTRIBUTION AT ANODIC AND AT CATHODIC SURFACES

If the surface treated is incorporated in the plasma-forming arc discharge circuit as its anode or cathode, this disturbs the thermic equilibrium of the thermal plasma in the region of the electrode voltage gradient.

In the anode voltage gradient region the electric field is strong enough to impart a considerable kinetic energy to the electrons even on their short free path lengths between successive colisions. Consequently, the difference between the translational temperatures of the electrons and of the heavier particles grows more marked. In the anode voltage gradient region, the electric field intensity is 50 to 100 times greater than in the electric arc column [3]; its intensity can be calculated from the anode voltage gradient U_a distributed within the thermal boundary layer, over a distance ε_a of the order of 10^{-4} m.

The electron temperature in the collision-prone zone of the anode voltage gradient region is determined as follows [2]:

$$T'_e = T_0 + \frac{m_0}{m_e} \frac{e\bar{l}_e E}{3k\delta}, \tag{13}$$

where E is the electric field strength, $\bar{l}_e$ — the mean free path length of the electrons, and δ — a coefficient expressing the proportion of energy transmitted by the electrons.

The increment $\Delta T'_e$ in the drift temperature of the electrons over the collision-free zone at an anodic surface can be computed, by analogy with equation (5), as

$$\Delta T'_e = \frac{3}{2} \frac{U_T e}{k}, \tag{14}$$

where U_T is the anode voltage gradient over a collision-free zone with a thickness equal to the mean free path length of electrons, $\bar{l}_e$.

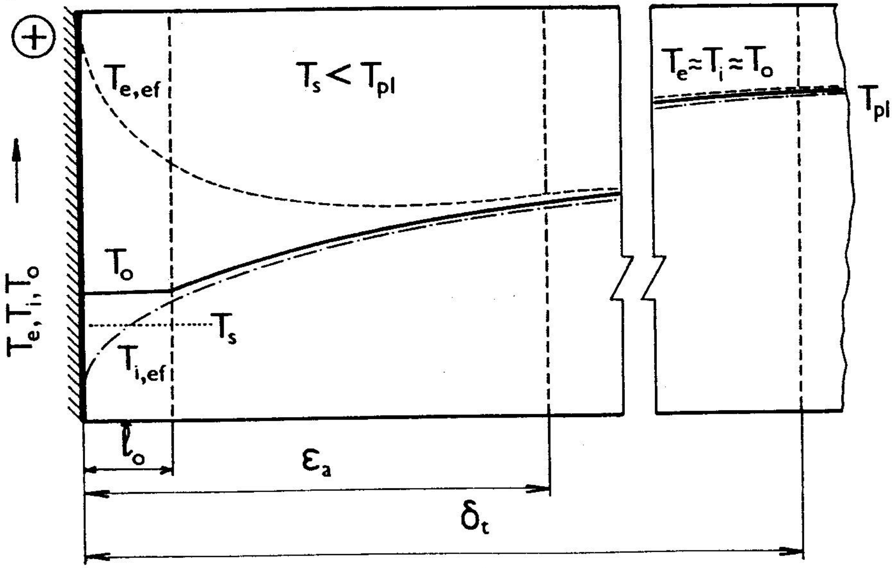

Fig. 3. Distribution of effective or r.m.s. translational temperatures of particles approaching an anodic surface; this distribution is typical for plasma remelting processes where the treated material bears a positive charge. ε_a — anode voltage gradient region; $\bar{l}_0$ — collision-free path length for electrically neutral particles; otherwise notation as in Fig. 1.

The effective or r.m.s. translational temperature $T_{e,ef}$ of those electrons which react with the surface is the sum of the translational temperature of electrons, T'_e, and the temperature increment $\Delta T'_e$ which corresponds to the drift energy the electrons gain in the collision-free zone of the anode voltage gradient region:

$$T_{e,ef} = T'_e + \Delta T'_e. \tag{15}$$

Ions migrate from the anode towards the cathode, and consequently take no part in interactions at the anode. Fig. 3 schematically represents the situation in a heterogeneous system, where the reacting surface forms the anode and is cooler than the thermal plasma acting on it.

If the reacting surface forms the cathode, the situation is very different, chiefly because the mass of the impacting ions approximates the mass of electrically neutral particles. The proportion of kinetic energy which ions impart to electrically neutral particles in every collision is given by the ratio $2m_i m_0/(m_i + m_0)^2$. This means that in the collision-prone zone of the cathode voltage gradient region, practically all the drift energy of the ions is transmitted to neutral particles. Fig. 4 shows a theoretical example of the distribution of the

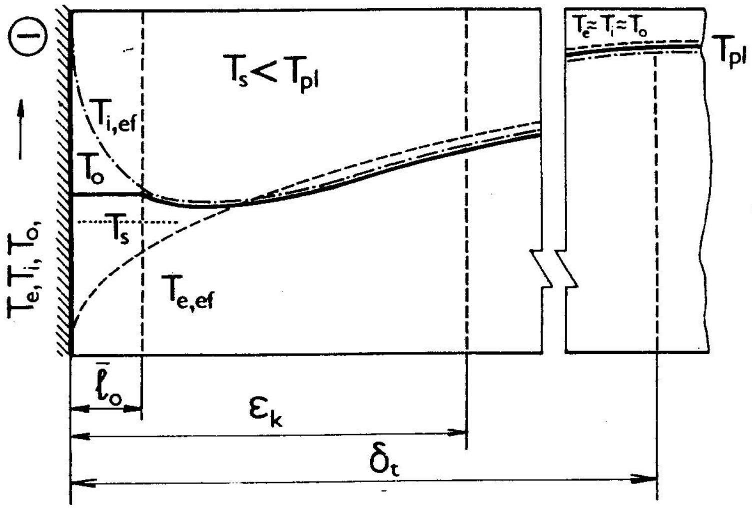

Fig. 4. Distribution of effective or. r.m.s. translational temperatures of particles approaching a cathodic surface; this situation is typical for plasma extractive and refining techniques where the charge polarity is negative. ε_k — cathode voltage gradient region; $\bar{l}_0$ — collision-free path length of electrically neutral particles; otherwise notation as in Fig. 1.

r.m.s. translational energies of electrons, ions, and neutral particles, at a cathodic surface in a system lacking thermal equilibrium, where the temperature T_s of the cathodic surface is lower than the thermal plasma temperature T_{pl}.

IV. CONCLUSION

A thermal plasma retains its thermic equilibrium and Maxwellian energy distribution only when it interacts with a surface from which the floating potential is abstracted as it forms. In such cases the equilibrium states and kinetics of the heterogeneous metallurgical reactions are characterized by the surface temperature T_s and by the temperature T_{pl} of the thermal plasma at a distance equal to one free particle path length from the surface.

If the reacting surface is electrically insulated, a floating electric potential arises on it and causes differences between the temperatures of the electrons, ions, and electrically neutral particles. The particles interacting with an electrically insulated surface at the temperature T_s possess potential energies corresponding to the thermal plasma temperature at the distance d_s from the surface.

If the reacting surface is incorporated in the arc discharge circuit as its anode or cathode, this causes each particle species to have its own effective or r.m.s. translational temperature. Neither the Boltzmann nor the Saha equations are applicable in calculations intended to reveal the composition of a plasma that interacts with an anodic or a cathodic surface.

NOTATION

E — Electric field strength (V m^{-1})

E_e, E_i, E_0 — Kinetic energies of electrons, ions, and electrically neutral particles interacting with the surface (J)

T_e, T_i, T_0 — Translational temperatures of electrons, ions, and electrically neutral particles in the free volume of the plasma (K)

T'_e, T'_i, T'_0 — Translational temperatures of electrons, ions, and electrically neutral particles at the outer surface of the plasma sheath (K)

$\Delta T'_e$, $\Delta T'_i$ — Changes in the translational temperatures of electrons and of ions in an electric field (K)

$T_{e,ef}$, $T_{i,ef}$, $T_{0,ef}$ — effective or r.m.s. translational temperatures of electrons, ions, and electrically neutral particles, respectively (K)

U_Z — Anode voltage gradient in the collision-free zone (V)

d_s — Plasma sheath (m)

e — Electron charge (1.6021×10^{-19} C)

k — Boltzmann constant (1.38054×10^{-23} J K^{-1})

$\bar{l}$ — Collision-free distance (m)

$\bar{l}_e$ — Mean free path length of electrons (m)

$\bar{l}_0$ — Mean free path length of electrically neutral particles (m)

v_e, v_i — Most probable drift velocities of electrons and of ions, respectively (m s^{-1})

ϑ_e, ϑ_i, ϑ_0 — Arithmetic mean velocities of the thermal motions of electrons, ions, and electrically neutral particles (m s^{-1})

δ — A coefficient expressing the proportion of energy transmitted by the electrons

ε_a — Dimension of the anode voltage gradient region (m)

ε_k — Dimension of the cathode voltage gradient region (m)

φ_s — Floating electrical potential (V)

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ПРОБЛЕМА РАЗНЫХ ТЕМПЕРАТУР В МЕТАЛЛУРГИЧЕСКИХ РЕАКЦИЯХ ПРИ УЧАСТИ ТЕРМИЧЕСКОЙ ПЛАЗМЫ

Когда металлургические реакции происходят в гетерогенных структурах, вклячающих плазму, плазменная температура существенно превышает температуру твердой или жидкой поверхности шихтового материала. В таких условиях термическая плазма сохраняет термальное равновесие и максвелловское распределение энергии только тогда, когда она взаимодействует с поверхностью, с которой извлекается плавающий электрический потенциал. Во всех остальных случаях, т.е. когда поверхность электрически изолирована или представляет собой анод или катод цепи разрядной дуги, генерирующей плазму, распределение энергии отличается от максвелловской модели, и эффективная температура поступательного движения электронов, ионов и электрически нейтральных частиц отличаются друг от друга.