Oscillation Modes of Slag-Metallic Bath Interface

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Assimilating the slag-metallic bath interface which is an electric double-layer and using the $mKdV^{\pm}$ equations, it is concluded that the oscillations of this interface are of the "cnoidal" type. The various oscillation modes (non-dispersive waves, wave packets, solitons, antisolitons, soliton packets) are obtained as degenerations of the "cnoidal" oscillations. Some considerations on practical applications importance are given.

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I. Introduction

In the case of the elaboration of certain alloys and metals (it is essential for steel), the slag has a decisive role in achieving a high degree of purity: small content of gases and impurities. For example, in the case of the metal purifying process by slag, chemical processes may occur between the reactants from the metallic bath on the one hand and the slag on the other hand. Let us consider the case of the slag-metallic bath interface processes, as an interaction between the ionic solution—as molten electrolytes—and the metallic bath. The chemical reactions between those two phases are topochemical reactions (see Ref. (1)) the efficiency of the chemical interaction depending on the size of the reaction surface.

The reaction surface is larger, the chemical interaction effect is stronger. So, the size of the contact surface between the slag and the metallic bath, *i.e.* slag-metallic interface, is important.

The presence of chemical elements in the metallic bath lowers the surface tension, the concentrating phenomenon of those elements at the superficial layer of the metallic bath occurs. So, the properties of the superficial layer of the metallic bath are modified. More precisely, the adsorption of the O^{2-} anions at the metallic bath surface determines its negative charge. At the same time, the slag is positively charged at the interface zone with the metallic bath, so an electric double-layer appears.

Let us explicitate the idea for a ferrous metallic bath. In this case the oxygen transfer from the gas-slag to the slag-metallic bath interface is achieved by the oxides of iron. In keeping with the molecular theory of slag (see Refs. (1) and (2)), at the slag-metallic bath interface the following processes take place:

FeO which is soluble both in slag and in the metallic bath

passes into the metallic bath according to the Nernst principle (see Refs. (1) and (2)) by an endothermic process:

One notices that there are two theories concerning the form of oxygen in the iron metallic bathes (see Refs. (1) and (2)). Oxygen is present either as singular oxygen, or attached to an iron atom as FeO. In the present context one admits that oxygen is attached to an iron atom as FeO. Consequently, the concentration difference between the FeO from the slag and the one from the metallic bath (FeO concentration from the slag is higher than in the metallic bath) causes the FeO diffusion from slag to the metallic bath. Between those two phases, a ratio between (FeO) activity and [FeO] activity builds

$$L_{FeO} = \frac{a_{(FeO)}}{a_{[FeO]}} \quad (4)$$

named the FeO coefficient distribution, which expresses the Nernst principle. In keeping with the slag ionic theory (see Refs. (1) and (2)) inside the slag the oxygen is in anionic form, (O^{2-}), resulted as basic oxides dissociation:

Iron is placed in the slag as cations (Fe^{2+}) and (Fe^{3+}). Since the cations (Fe^{3+}) have an high electrostatic potential they determine the polarisation of some of the oxygen anions from the slag forming complex anions:

The free oxygen anions and the FeO_3^{3-} ones accumulate at the slag surface and thus between the interfaces gas-slag and slag-metallic bath creates a potential difference which determines the diffusion of O^{2-} and FeO_3^{3-} towards the slag-metallic bath interface, where in contact with iron it determines the generation of the Fe^{2+} cations according to the reaction (see Refs. (1) and (2)):

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The O^{2-} anions, by passing into the metallic bath, determines the development of an electrical double layer. The superior part of the electric bath charges negatively and the inferior one, of the slag layer, positively. The continuous passing of the O^{2-} anions is impeded, the O^{2-} anions being repelled by the potential barrier because the transition through the interface means: $(O^{2-}) = [O] + 2e$.

In the metallic bath passes a significant quantity of oxygen, since together with it passes the iron too according to the mechanism:

Thus it results that not any oxide which emanates oxygen anions in the slag has an oxidising character for the metallic bath, but only those which contain cations soluble in iron—if those oxides are soluble in iron. This condition is achieved only by FeO and less by MnO, CaO, MgO, etc., which means that a slag without FeO has no oxidation power—it cannot be used to loose the metallic bath.

The presence of particles with the same charge determines the increasing tendency of the surface of those two phases from the interface zone (the particles with the same charge being scattered). Consequently, the interfacial tension is lowered.

Generally, the variation of the interfacial tension, $d\sigma$, is given both on the electric double-layer potential, ϕ , and on the chemical potential, μ_i , through the relation:

$$d\sigma = -\varepsilon d\phi + \sum_{i=1}^n \Gamma_i d\mu_i, \quad (12)$$

where ε is the superficial charge density of the double layer and Γ_i represents the absorption coefficient of the i -th element. When the chemical composition of the phases in contact is constant ($d\mu_i = 0$), relation (12) transforms into the Lippman relation:

$$\frac{d\sigma}{d\phi} = -\varepsilon. \quad (13)$$

Taking into account the above observations, ε defines the superficial charge excess (electrons) from the slag-metallic bath interface (see Ref. (1)).

Assuming the variation of the surface tension is due to considered electric double-layer potential (see relation (13)—the concentrating phenomenon of the chemical elements which increases the surface tension is permanent, the infinitesimal variation of the surface tension with the activity, $d\sigma/da_0$, where a_0 is the activity, being negative) in this paper, using the $mKdV^\pm$ equations, various oscillation modes of the slag-metallic bath interface are given: plane waves, packets of waves, soliton, antisoliton, packets of solitons. From our analysis it results that “the oscillation modes” may be perturbed by certain external exciting factors (electric, magnetic and ultrasonic fields). The aim of this analysis is to find the conditions for a maximum contact surface between the two phases, i.e., the

maximum reaction efficiency.

II. The Mathematical Model

Taking into account Ref. (1), at the surface of separation between the slag and the metallic bath, a double-layer forms. Assimilating, as in Ref. (3), the double layer with a two-fluid model with superficial tension, the interface dynamics will be described by the modified Korteweg-de Vries equation ($mKdV^+$), (see Refs. (3) and (4)):

$$\frac{\partial \phi}{\partial t} + a\phi \frac{\partial \phi}{\partial x} + b \frac{\partial^3 \phi}{\partial x^3} = 0, \quad (14)$$

where ϕ is the electric double-layer potential and a , b are coefficients depending only on the nature of the electric double-layer (that is, on the nature of slag-metallic bath interface) and on the type of elementary processes evolving inside it. Equation (14) expresses the fact that non-linear effects, $(a\phi(\partial\phi/\partial x))$, and dissipative ones, $(b(\partial^3\phi/\partial x^3))$, implies the time dependence of the potential.

The adimensional equation of the surface tension variation at interface:

$$\frac{\partial \psi}{\partial \tau} + \psi \frac{\partial \psi}{\partial \xi} + \frac{1}{\theta^2} \frac{\partial^3 \psi}{\partial \xi^3} = 0, \quad (15)$$

where

$$\psi = \frac{\sigma}{\sigma_0}, \quad \xi = \frac{x}{l}, \quad \tau = \frac{t\sigma_0 a}{\varepsilon l}, \quad \frac{1}{\theta^2} = \frac{b}{a\sigma_0 l^2}, \quad (16)$$

results from eq. (14) by using a standard “recipe” given in Ref. (1), associating the surface tension to the potential ϕ , ($\sigma \sim \varepsilon\phi$). In the above relations (σ , l) are the interface specific parameters (see Ref. (4)).

By using the method given in Ref. (5), the perturbative solutions of eq. (15) are of the form:

$$\psi = \psi_0 + A cn^2[\alpha(\xi - c\tau); s] \quad (17)$$

with

$$c = \psi_0 + \frac{A}{3} \left(2 - \frac{1}{s^2} \right), \quad \alpha = \frac{\theta}{s} \left(\frac{A}{12} \right)^{1/2}, \quad \psi_0 = \text{const.} \quad (18)$$

In these relations A is the perturbation amplitude and cn is the Jacobian elliptic function with modulus s (see Ref. (6)). Equation (17) shows that the variation of σ at the interface is of “cnoidal waves” type, in other words, the interface acts like a non-linear lattice (a Toda lattice), (see Ref. (7)).

In Fig. 1 the “cnoidal waves” are plotted for $u = \alpha(\xi - c\tau)$.

Since $\theta^2 \sim a/b$, it results that for small θ values the scattering effects appear before the non-linear ones, while for great θ values the situation inverts. In this context one can discern the following degenerations:

(i) for $s=0$ eq. (17), taking into account the Refs. (6) and (7), reduces to the non-dispersive wave:

$$\psi = \psi_0 + A \cos \left[\frac{\pi}{l} (x - ct) \right]; \quad (19)$$

Fig. 1 Cnoidal oscillation modes for the slag-metallic bath interface.

Fig. 2 Degeneration of cnoidal oscillation modes in wave packets (low amplitude waves).

(ii) for $s \ll 1$, *i.e.* for small θ , eq. (17) reduces to the “wave packet” (see Ref. (2)). In Fig. 2 is plotted the solution of eq. (17) for $\theta=2$.

(iii) for $s=1$, eq. (17) reduces to the soliton:

$$\psi = \psi_0 + A \sec^2 h^2[\alpha(\xi - c\tau)] \quad (20)$$

of parameters

$$\alpha = \theta \left(\frac{A}{12} \right)^{1/2}, \quad c = \psi_0 + \frac{A}{3}. \quad (21)$$

In Fig. 3 is plotted the soliton solution, big amplitude perturbation, $A = \text{const.}$ and width $\sim (12/A)^{1/2}$ (see Ref. (8)).

(iv) for $s \rightarrow 1$, *i.e.* for great θ , eq. (17) reduces to the “soliton packet” (see Ref. (2)). In Fig. 4 is plotted the “soliton packet”, for $\theta=16$.

If the non-linear term in eq. (15) has the “−” sign, *i.e.* for the *mKdV* equation, the solution of the problem changes to the form:

$$\psi = \psi_\infty - A' \text{cn}^2[\alpha(\xi - c\tau); s] \quad (22)$$

where

Fig. 3 Degeneration of cnoidal oscillation modes in solitons (high amplitude wave).

Fig. 4 Degeneration of cnoidal oscillation modes in soliton packets (high amplitude waves).

Fig. 5 Degeneration of cnoidal oscillation modes in antisoliton (high amplitude wave but in opposite phase with the soliton).

$$c = -\psi_\infty + \frac{A'}{3} \left(2 - \frac{1}{s^2} \right), \quad \psi_\infty = \text{constant}. \quad (23)$$

For $s=1$, eq. (22) degenerates into the antisoliton:

$$\psi = \psi_\infty - A' \sec^2 h^2[\alpha(\xi - c\tau)] \quad (24)$$

where

$$c = -\psi_\infty + \frac{A'}{3}. \quad (25)$$

The antisoliton given by eq. (24) is shown in Fig. 5. It is a big amplitude perturbation, $A' = \text{const.}$ and width $\sim (12/A')^{1/2}$ (see Ref. (8)). The perturbations in the soliton and in the antisoliton are in opposition of phase (see Ref. (8)).

III. Relationship between Oscillation Mode and Reaction Behavior at the Slag-Metallic Bath Interface

At the slag-metallic bath interface there are two processes which are interrelated: the forces of interphasic tensions have the tendency to decrease the area of the separating surface, while into the double layer, thank to the electrostatic repulsion between the particles with the same charge, the area of separating surface has the tendency to increase. In this case, if a voltage operates, from outside, then one of oscillation modes of the interface (train of waves, solitons, soliton packets, etc.) will be excited. This will result in neutralising of the charges from the interface and hence in decreasing the interphasic tension. Thus, by changing permanently the area of the interface, various reactions between the slag and the metallic bath can be controlled. Such reactions are: desulphurization, dephosphorization, diffusion of oxygen from the slag into the metallic bath, reduction of the oxides from the slag by the chemical elements from the metallic bath by the slag, etc. Heat transmission from the heat source to the metallic bath by the slag can be influenced, too. Let us analyse the direct influence of surface changing on the kinetics of the certain processes at the interface. Thus, concerning the desulphurization, if the slag is accepted as prevailing, the rate of desulphurization (v_s) (see Ref. (1)) is:

$$v_s = \frac{D_s A}{\delta} [(S)_E - (S)_V], \quad (26)$$

where D_s is diffusion coefficient of sulphur through the slag, A is the area of contact surface between the slag and the metallic bath, $(S)_E$ is the average concentration of sulphur in the superficial layers of the slag, $(S)_V$ is the average concentration of sulphur in the volume of the slag and δ is the thickness of the slag layer. Thus, possibility to increase the desulphurization rate is to increase the interface area. By the exciting of the weak modes of oscillation, the increase of the desulphurization rate is relative

small, while by exciting the strong modes, that one is big.

The numeric simulations show that for $\theta=2$ the relative increase of the surface in comparison with the plane case is of 1.2 and for $\theta=16$ the increase is of 3.1 (see Ref. (9)). Since in the electric spark heating furnaces the area of the slag-metallic bath interphasic surface increases, by exciting it, three times compared to the case when the surface is not excited (see Ref. (1)), it results that in such a situation only the strong modes are excited. Upon these last ideas we shall go back in a future paper.

IV. Conclusions

The present analysis, shows the fact that the surface tension oscillations at the interface are at "cnoidal" type. These oscillations degenerate in non-dispersive waves, wave packets, soliton, antisoliton, soliton packets, on the ratio between the dispersive term and the non-linear one, therefore depending on the adsorption phenomena of the chemical elements which lowers the surface tension.

Because the maximum variation of the interface surface of the slag-metallic bath is given by a train of solitons, it results that a maximum efficiency of the slag-metallic bath interaction phenomena (chemical reactions) is obtained by perturbing this oscillation mode.

The above situation may be achieved practically in the case of the electric-arc furnace used for elaboration of steel, by using an external electromagnetic field.

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