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The role of metal and slag films stabilization phenomena with respect to clean steel

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The conditions of a stability of metallurgical films on a surface of solid on the basis of classical regularities of a thermodynamics are considered. For specific conditions of metallurgical processes the basic equations relevant to non-metallic inclusions (product of steel killing) migration and transfer through the interface boundary of metal-slag are obtained.

The basic criteria equations of conditions of stability of metallurgical dispersed systems are developed in view of films formation. The probable thermodynamics reason of wetting due to formation of stable films are discussed. The experimental measurement of thin and thick films elastic resistance for metallurgical systems are carried out and the results are discussed. The presence of a wetting thick film increases stability of dispersed systems (facilitates an inverse implication of non-metallic inclusion in a melt) due to a barrier effect of wetting films. The quantitative evaluations of non-metal inclusion stability for steel in contact with any metallurgical slag are carried out. The results are in accordance with technological experience.

Keywords: Inclusion removal, Film thermodynamic, Slag-metal dispers system

Introduction

A steel refining reduces in formation of a dispersible system: suspensions of solid or emulsion of liquid inclusions in a killed liquid metal. The removal of large particles happens during first of minutes. The removal of inclusions with the size 10–20 microns requires tens of minutes and frequently practically does not happen in time from an issue of steel in a ladle before an ingot solidification[1]. The regularities of removal of inclusions are connected to capillary forces and thermodynamic stability of wetting films and adsorption layers on a surface of solids and fluids. The conditions of stability influence on processes of integration of inclusions in steel and their passage through the intersurface boundaries.

The role of capillary phenomena in a processes of metals refining and, in particular, at an exit of inclusions on the interface boundaries, is discussed in a series of works[2–5]. The problem of stability of films is important also for a technology of composite and cermet materials production with use of such processes, as impregnation by a liquid phase, sintering, melting of cermet electrodes etc. The problem consideration has also basic theoretical value. The mathematical methods of thermodynamics of thin films[6] are applicable to explanation of layers stability of metal solutions in phenomena of coagulation in melts or at an exit of non-metal particles on the boundaries metal-gas or metal-slag. The problem of films stability could be reduced to reviewing a phenomena of wetting.

Thermodynamics of solid wetting

Frumkin[7] considers the problems of the process of solid wetting. However, in all considered cases an intersurface tension $\sigma^{\alpha\beta} > \sigma^{\beta\gamma}$ (the unary indexes indicate to phases: α-solid or liquid inclusions, β-gas, γ-metal; double-to the boundary between phases). For metallurgical systems the practical interest is represented by conditions of wetting at $\sigma^{\alpha\beta} < \sigma^{\beta\gamma}$. It is realized at contact of liquid metal to majority of high temperature compounds such as oxides and nitrides. A tension of a thick film: $\sigma_{fT} = \sigma^{\alpha\gamma} + \sigma^{\beta\gamma}$ always it is more then $\sigma^{\alpha\beta}$, therefore, such condition are unstable. A realization of an equilibrium condition of massive liquid only with adsorption layer film of molecular sizes (with thickness ℓ_A, Figure 1 A, curve 1) is possible in this case. Frumkin has justified a possibility of formation of extremum of a film tension (σ_f) with a decrease of its thickness. Derjaguin[8] has explained existence of extremums by origins of disjoing pressure (Π) a variable sign in thin wetting films. In an outcome a tension of thin film is determined by the formula:

$$\sigma_f = \sigma^{\alpha\gamma} + \sigma^{\beta\gamma} + \left(\sigma_{fT} / \ \right) = \sigma^{\alpha\gamma} + \sigma^{\beta\gamma} + \Pi \qquad [1]$$

Presence of area $\Pi < 0$ on a curve of Π modification with a thickness of films is defined experimentally[9] (Figure 1, B). It gives an isotherm of σ_f with two extremum (Figure 1 A, curve 2). On a line $_E$ ... $_M$ in the field of thick films

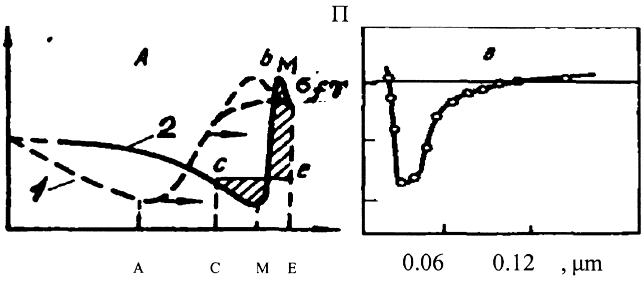

Figure 1. Typical isotherm σ_f (A) and Π (b) as a function of film thickness ℓ

(σ_f/∂_) < 0. A film of fluid in this interval of a thickness has a practical stability, though these states are metastable. Passage from this state in a labile, on which (σ_f/_) > 0, is connected to an expenditure of work being energy of activation of passage in a labile state. In an equilibrium with a volumetric phase is a film of a strictly defined thickness, defined by point C on a curve σ_f. The equilibrium thickness of a film is determined from a condition of equality of chemical potentials (μ_i) in volume and film. The potentials discover by an integration of Gibbs equation along a curve σ_f:

$$\mu_i^T - \mu_i^C = \sigma_f^C\left(1/\ _E - 1/\ _C\right) - \sigma_f d(1/\ ) = 0 \qquad [2]$$

The equality is valid, if the squares shaded on Figure 1 A are equal (lie above and below line CE). The possibility of thermodynamically stable film formation on a descending curve CD follows also from the analysis of the basic Equation [1] for Π. The condition from a point D (min) up _= 0 is steady, as at Π < 0 and (∂Π/∂_)< 0 from the Equation [1] can be obtained a condition of a stability:

$$\left(\sigma_f / \ \right) < 0 \qquad [3]$$

Thermodynamics of inclusions removal

Thermodynamic possibilities of the process of inclusions passage from volume of steel on an intersurface of a melt[4] with use a difference of the Helmholtz (F) and Gibbs (G) potentials as a common conditions of direction of processes are as follows:

$$(\Delta F)_{T,\,V,\,ni}\ \ 0 \text{ and } (\Delta G)_{T,\,P,\,ni}0 \qquad [4]$$

Let's consider a system, in which the concentration of inclusions of a dispers phase is rather small to neglect processes of coagulation, and the size of particles is rather small (10–20 microns and less) to neglect gravitational forces. In conditions, when volume and temperature are fixed, a stability criterion of such system is ΔF at transfer of a non-metal particle from volume of liquid steel on interface[4,6]. Let's define ΔF for two sequential equilibrium condition of non-metal inclusion (α-phasa) with a spherical interface. In the first condition the inclusion is inside a metal phase (γ), in second - on an interface of metal with a gas phase or slag, but the boundary (αβ) is separated from them by a film of metal (f), Figure 2. Considering homogeneous and incompressible inclusion, a difference of a free energy of a system is expressed as follows:

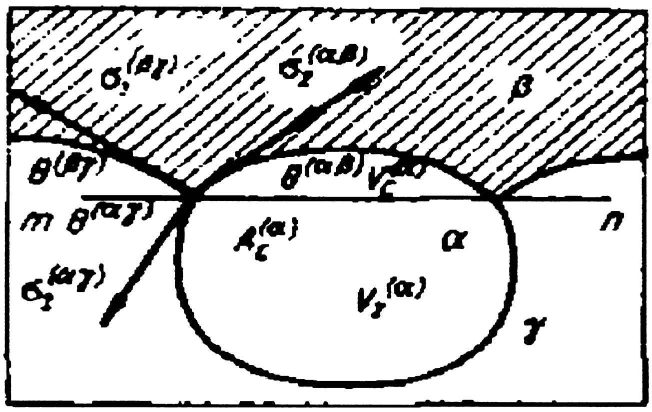

Figure 2. Scheme of the non-metal particle (α-phase) on interfacial boundary metal (γ-phase)–slag or gas (β-phase)

$$\Delta F = -V^\alpha P^\alpha + \sigma_f A_2^{\,f} + \sigma^{\alpha\gamma}\left(A_2^{\alpha\gamma} - \acute{A}_1^{\alpha\gamma}\right) + \sigma_f^{\ \beta\gamma}\left(A_2^{\beta\gamma} - A_1^{\beta\gamma}\right) + n_i\left(\mu_{i2} - \mu_{i1}\right) \qquad [5]$$

Here i - concerns only to a non-metal phase, 1 - to a position of inclusion inside metal, 2 - to a position on the boundary of phases αβ. The tension of a film σ_f is determined by the Equation [1]. Neglecting an adsorption and distortion of a surface in a place of a surface of metal contact with a film ($\delta A^{\beta\gamma} \approx 0$), and applying geometric relations Figure 2:

$$A_2^{\alpha\beta} A_2^f = 2\pi\left(r_2^{\alpha\beta}\right)^2\left(1-\cos\theta^{\alpha\beta}\right); \quad A_c^\alpha = \pi\left(r_2^{\alpha\beta}\right)^2 \sin^2\theta^{\alpha\beta} \qquad [6]$$

The difference of the Helmholtz free energy in the considered process referred to unit of a surface of a metal film, covering inclusion, is assume the form:

$$\Delta F_A = \sigma^{\beta\gamma}\left[\left(1+\cos\theta^{\alpha\beta}\right)/2\right] + \Pi\ell \qquad [7]$$

The Equation [7] allows to carry out the quantitative definition of disjoing pressure of a metal film, if are known $\sigma^{\beta\gamma}$ and $\theta^{\alpha\beta}$. A measurement Π represents large difficulties, therefore we shall make an approximate evaluations. In case of full wetting a thick films of metal are stable , i.e. the inclusion spontaneously passes in volume of metal ($\theta^{\alpha\beta}$ 0). From the Equation [7] is obtained, that the positive value of disjoing pressure should be decrease (Π→0). The obtained requirement is equivalent to a condition of a spontaneous thickening of wetting film[7], stipulated by a decrease of its tension in this process (see. Figure 1, curve 2). In case of formation of thin wetting films (partial, limited wetting with formation of a final equilibrium angle, see curve 2, point C) the inclusion can extrude a film up to some limit with formation $\theta^{\alpha\beta}$ close to 90°. Such picture observed and discussed in works5,10. In this case possibility of a realisation of the process of an inclusion passage on the intersurface is estimated by an approximate criterion obtained from the Equation [7]:

$$K = 0.5\sigma^{\beta\gamma} + \Pi\ell \qquad [8]$$

The process is possible at K < 0, i.e. the equilibrium existence of a film is possible at a final negative value of a disjoing pressure $\Pi \le (-0.5\sigma^{\beta\gamma})$/_. The presence of a wetting film can facilitate an inverse implicating of inclusions in volume of a melt from the interfaces. The practical stability of a dispersed system is increased. Thus, the origin of stable wetting films renders a barrier effect to exit of non-metal inclusions (products of a steel killing) through the interface boundary.

Experimental study of a stability of a films of liquid metals

Information about a possibility of formation of wetting films and their barrier effect on non-metal inclusions of various structure have received with the help of measurements by a weigh method of horizontal plate in melts. The experiment consists of a measurement with the help of spring scales (sensitivity ± 1.10^{-5} g) of a force, operating on a plate from non-metal materials moved from volume of a metal melt to its surface. Transference of a plate fixed with the help of micrometric screws of an optical microscope to within ± 1 micron.

The singularity of experiment is, that the metal wetting film during a measurement can take a position above than level of liquid(Figure 3, A). Therefore method does not allow immediately to measure a thickness of wetting films, but enables to define a force of an elastic resistance of a film in function of transference. The data of measurements of a force, operating on non-metal inclusions at the interface boundary in liquid alloys based of Ni and Fe (with containing C 0,5 … 1.9% mass) are represented on Figure 3. In all experiences surface tension of liquid metal ($\sigma^{\beta\gamma}$) > ($\sigma^{\alpha\gamma}$) - surface tension of any used non-metal material. The obtained data are described by the considered basic 3 types of isotherms of a metal film tension in function of a thickness (Figure 1). The 1-st: Figure 1, A, curve 1 (isotherm with a maximum)- partial, limited wetting with formation of massive films down to thick. The situation is the same with the graph in Figure 3. The curve 1 is characteristic of wetting ZrC and TiC by nickel at $\sigma^{\alpha\beta} > \sigma^{\beta\gamma}$ (full wetting at an equilibrium of a massive phase with adsorption layers). In these cases a force of a resistance is increased as a plate approaches the interface of a melt before rupture of a wetting film, and then up to a separation from a surface. The curve 7 is typical for wetting slag systems by thick films of Fe-C alloys. The 2-nd: Figure 1, A, curve 2 (isotherm with a maximum, compressed due to effect of disjoing pressure). This picture is in accordance with graphs in Figure 3. The curve 6 is typical for wetting slag systems by a nickel. It is illustrated the equilibrium of massive metal phase with a wetting thin film of metal, that is exhibited as an inflection on curve 6. Here force of a resistance will increase on a segment TM (Figure 1, isotherm 2) in area of thick films stability. After break of a thick film the resistance drops. The decrease of a thickness of a film is occurred up to equilibrium thickness in a point C. Then the resistance of a thin film increase before break and resistance of capillary forces increase up to a separation of a plate. The 3-rd: Figure 1, A, curve 1 (isotherm without maximum)-wetting is absent, the plate is pushed out on a surface of a melt after formation of a film and spontaneous it of break. Figure 3, curves 2–5 characterize pushing of a plate from melts Fe-C: 2-TiO_2 (is obtained by a sintering); 3-SiO_2; 4–MgO; 5-$Àl_2O_3$. For an elimination of any dynamic effects the slags beforehand reduced in an equilibrium with a melt of metal. Thus, from all investigated systems only on a products of Mn and Si killed Fe-C melt and BOF-slag in Ni were formed the stable metal films hindering removal of inclusions from a liquid melt. Experimentally is revealed but it does not mean, that the killing products by silicon and aluminium uniformly do not test a barrier effect of surface layers. The metallurgical practice gives examples of the worse removal of inclusions after killing by silicon. It is explained by propensity to formation complicated inclusions, containing oxides of iron.

Influence of slags on stability of inclusions - steel disperse systems

It is possible to carry out the evaluation of influence of slag covering metal, under the simplified formulas. If the inclusions go out on the interface boundary metal-slag, happens the solution them in a slag[5] and $\sigma^{\alpha\beta}$ _ 0, and $\theta^{\alpha\beta}$ 90°. Therefore, the formula [7] can be writing as:

$$K = -0.5\sigma^{\beta\gamma} - \sigma^{\alpha\gamma} \quad [9]$$

Similarly for liquid inclusions equation[4]: $K = \sigma^{\alpha\beta} - \sigma^{\beta\gamma}(1 + \cos\theta^{\alpha\beta})/2 - 0.3\sigma^{\alpha\gamma}$, we shall write as:

$$K = -0.5\sigma^{\beta\gamma} - 0.3\sigma^{\alpha\gamma} \quad [10]$$

Let's consider within the framework of the simplified criterions [9,10] influences to a stability of a suspension of inclusions in steel of a structure of technological slags composition. The equations allow to estimate a stability of suspensions and emulsions derived by killed steel inclusions and drops of slags at an exit on an interface metal - slag, and ability of slags to pass in metal. The slags

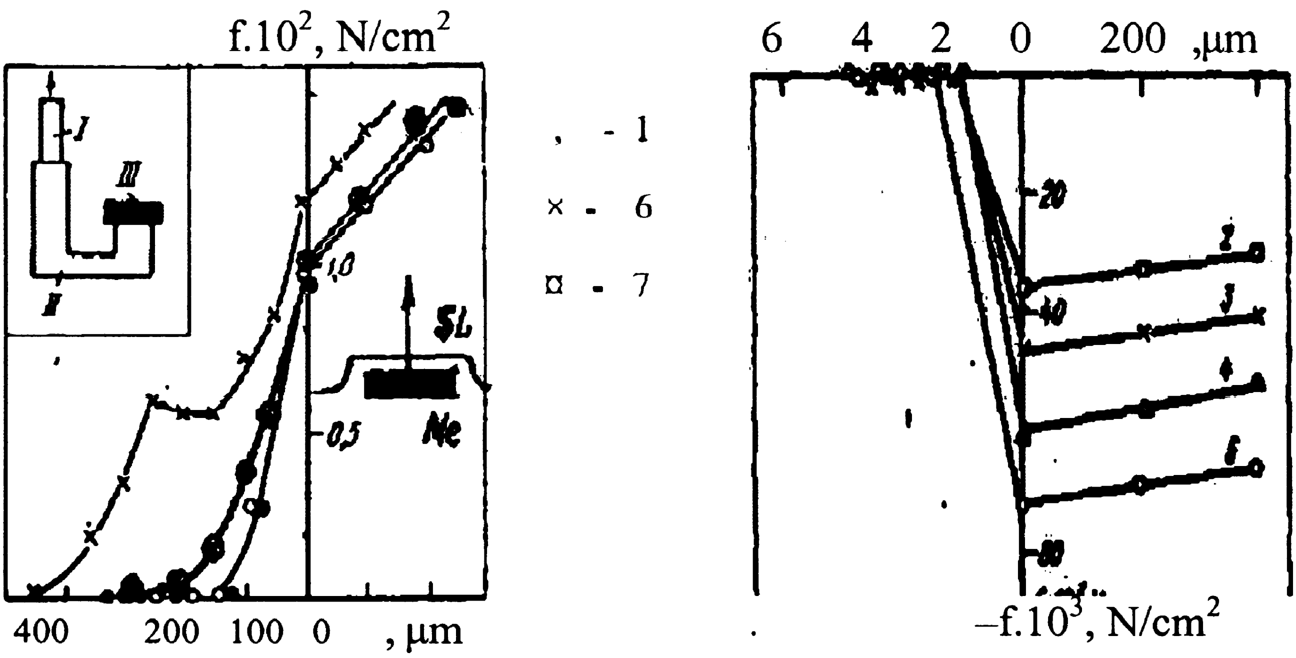

Figure 3. Results of experimental measurement of the resistance of liquid metal films: I-W rud, II-element fromMgo, III-experimental plate. 1-full wetting by liquid Ni-metal on ZrC andTiC plates; 2–5-Fe-C melts not wetting: 2-TiO_2 sintered, Fe (1,9%C), 1470°C; 3-SiO_2 melted, Fe(0.3%C), 1500°C; 4-MgO, Fe(1.22%C), 1500°C; 5-Al_2O_3, Fe (1.22%C), 1500°C; 6-wetting by liquid Ni films on metallurgical slag particle (50%FeO, 21.5%SiO_2, 20%CaO, 8.5%Al_2O_3); 7-full wetting by liquid Fe (0.1%[O]) on slag (43.8% MnO, 23.8% FeO, 32.4% SiO_2)

composition is indicated in a Table I. The results of calculations for a series of industrial slags are given in a Table II.

For all considered systems the solid inclusions Al_2O_3 are removed from steel more preferable (K less). The suspensions of these particles in steel have the least stability. With a decrease of a content Al_2O_3 in liquid inclusions the stability of emulsions is increased. Under white electro-steelmaking and other refining slags with a high content Al_2O_3 and CaO metallurgical suspensions and the emulsions are less steady, than under carbide and BOF slags, that will be agreed a technological data.

In all cases, as follows from a Table II, carbide and BOF slags as inclusions in steel, will form the steadiest emulsions. The data also are confirmation of the technological recommendations of using Na_2O and Na_3AlF_6 for improving a desulfurizing properties of slags. Presence of these compounds in particles of slags and inclusions in steel does not influence a modification of stability of emulsions (see Table II, slags 3, 4, 7, 13, 14). All considered refining slags have approximately identical refining, absorption and of emulsion destabilisation ability for wide list inclusions and slags particles in steel. In this sense the experience of application for refining of cheap blast and OH- processes slags is justified.

Conclusions

The mathematical methods of a thermodynamics of thin films are applicable to explanation of stability of layers of metal solutions in phenomena of coagulation in melts or at an exit of non-metal particles on the boundaries metal–gas or metal–slag. The problem of the stability of films could be reduced to a phenomena of wetting: formation of extremum of a film tension (σ_f) with a decrease of its thickness due to existence of disjoing pressure (Π) a

Table I
Composition of technological slags and killed steel inclusions

No.	Title of slag	Composition, %mass					
	Electro-steelmaking	Al_2O_3	SiO_2	CaO	FeO	MgO	Other
1	White	3.0	20.0	47.0	-	10.0	20 CaF_2
2	Carbide	-	-	-	-	-	-
3	Synthetic	42.5	-	53.3	-	4.2	-
4	OH-process (scraps)	28.0	51.3	16.1	0.8	3.3	0.5 Na_2O
5	BOF – 1	-	8.4	21.6	70.0	-	-
6	BOF – slag	-	4.8	37.9	57.3	-	-
7	Synthetic	45.5	-	54.5	-	-	-
8	Inclusions of killed steel X15	41.0	33.4	19.3	0.70	5.6	-
9	The same	23.0	56.1	13.5	0.45	5.0	2.3 MnO
10	The same	7.0	59.4	22.0	0.70	7.1	3.4 MnO
11	Crystal (solid)	-	100	-	-	-	-
12	Experimental	41.0	10.0	49.0	-	-	-
13	For desulphurization	44.1	-	52.9	-	-	3 Na_3AlF_6
14	The same	42.8	-	51.2	-	-	6 Na_3AlF_6
15	Corundum (solid)	100	-	-	-	-	-

*Is obtained from slag by 1 addition of calcium carbide up to 3.21 %.

Table II
A value of K for killed steel inclusions under industrial slags

No. of slag	$\sigma^{\alpha\gamma}$ mJ/m²	- K, mJ/m², for steel in slags N			
		1 (1250)	2 (690) Steel X15	3 (1310)	4 (1110) *
8	1300	2550	1990	2610	2400
9	1200	2450	1890	2510	2300
10	910	2160	1600	2 220	2010
1	1250	2500	1940	2560	2350
2	690	1940	1380	2000	1790
4	1110	2360	1790	2420	2210
*In brackets the values of an inter surface tension sbg, mJ/m² on the metal– slag boundary.					
No. of slag	$\sigma^{\alpha\gamma}$ mJ/m²	- K, mJ/m², for steel in slags N			
		7 (1130)	5 (310) Fe-C (0.04 %mass)	6 (360)	
15	2260	3390	2570	2620	
12	1120	2250	1430	1480	
13	1130	2260	1440	1490	
14	1110	2240	1420	1470	
11	800	1930	1110	1160	
5	310	1440	620	670	

variable sign in a thin films makes an inclusions wettable by metal. The origin of stable wetting films renders a barrier effect to passage of non-metal inclusions (products of a steel killing) through the interface boundary. The stability of emulsions and suspensions is determined, in basic, relation of intersurface tensions of contacting phases.

For simple, but practically important case of removal of non-metal inclusions of steel and inclusions of technological slags the approximate criterion, permitting to estimate a possibility of removal of these inclusions, and also absorption ability of slags is obtained. By results of the analysis the removal of inclusions formed in Al killed steel more probable, than inclusions by mixtures containing silicon and manganese, that agrees with technological experience. The absorption ability of cheap slags BOF and OH-process, and also slags with addition the desulfurizing components (Na_2O, Na_3AlF_6) is approximately the same, as refining synthetic ones.

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