FEW TEORETIC ELEMENTARY NOTIONS REQUIRED FOR CHARACTERIZATION OF METAL MELT AND APRECIATION OF BEHAVIOR AT INTERFACE DURING CASTING

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ABSTRACT:
Surface tension is one of the properties of metal melt, which depends on two other properties, cohesion and adhesion. Atomic-scale phenomena can be regarded as if atoms or molecules within a substance are spaced sufficiently small, then each of them is surrounded by a field of forces, which form a system equivalent to zero. Forces are forces of cohesion, named "Van der Waals" forces.

1. INTRODUCTION

To separate atoms or molecules of the same type, some others must consume a mechanical work, it carry the name mechanical work of cohesion. The force that opposes atoms separation or molecules of that substance reported at length shall be known as surface tension (σ). Adhesion is the force of attraction between atoms or molecules that are in different phases. It is characterized by the work that needs to be done to separate the two phases in contact with the surface contact unit. The properties of surface flows have an important role, which include both surface tension and inter-phase and moistening phenomena.

2. DOCUMENTARY STUDY

Understanding the nature of surface tension in metals and alloys requires a profound study of this phenomenon. When two phases, for example liquid and gas are in direct contact, between them it forms a very thin separation layer, called the interface or inter-phase or phase separation. The interface properties differ from those of phases in contact. In this area the number of atoms and distribution functions of their energy is changing continuously, from the value which they have in melt, to the one which they have outside the melt. While atoms are leaving the surface, entering in liquid or evaporating outside the liquid, other atoms are replace. Stationary time of atoms at the liquid surface is very short, but it's longer than the remaining sibotaxis groups of atoms inside the liquid. At the melt surface occur a flux of collectivized electrons, which tend to get of the environment, but positive ions pull them back into the melt.

Metal melt surface are covered by a thin layer of liquid with negative loads, under which by a certain depth of atomic radius order, it's located a layer with compensating positive electrical loads. The two layers form a double layer with a thickness of interaction radius of an atom order. This double layer acts as a electrical condenser as a barrier, preventing, at least partially, the outgoing of electrons molten metal.

An atom in the melt, under the double layer, at a distance greater than the range of inter-atomic forces is surrounded by a field of forces, which together with its own forces form a system equivalent to zero. It has an effect of mutual annihilation of the forces of interaction between atoms, which allows free movement, as there is cohesion between them.

So the forces of interaction between atoms which belong to melt and the gas from the interface, will be much smaller than the forces of interaction between atoms on the surface of the liquid and the liquid inside.

If we consider a point particle (N) at a depth (X) less than the radius of the sphere of action of inter-atomic forces (r), figure 1, all atoms which are located in the EGF ABFE sector, will draw down N atom, while atoms in the ABCD and CHD sector, N atom will be attract upwards.
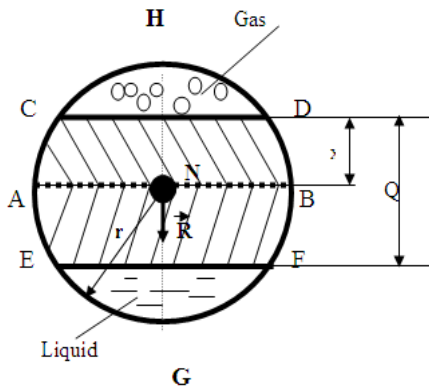
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Figure 1. Schematic representation of double layer Q, between liquid and gas phases

The ABCD and ABFE being equal, it can be assumed that the atoms contained in these, cancel each other so that the atom N is drawn down only in the liquid by atoms in the EGF because the forces of interaction between atoms in liquid are much higher than those between atoms in the gas CDH. It follows that the resultant $\vec{R}$ of forces acting between atoms in liquid and gas and the atom N is facing towards the liquid, being normal to the surface of separation.

Because at the apparent liquid surface, are located a very large amount of atoms N, acting on their resultant R of the interaction forces, normal to the surface and directed into the liquid, they act as an elastic membrane which surrounds the liquid and exercise forces on it, which, reported to the surface pressure is the internal liquid.

Energy between the two contact surfaces of the different phases shall be known as the Gibbs energy, and the change at constant temperature and pressure, reported to the surface between both phases shall be known as inter-facial surface tension or tension Gibbs.

Consequence that the attraction of atoms from metal melt surface, produces forces directed towards the inside, is that the surface free energy is greater than the one from inside. The absence of this excess energy, surface separation would not be stable, would degrade at the lowest energy state of fluctuation, the two phases in contact would disperse to another one.

To form a surface should be consumed a mechanical work needed to bring the atoms of the liquid on the surface, the same thing for the surface growth. Consuming a mechanical work it's decreasing the surface free energy.

3. ANALYSIS, INTERPRETATION - EXPERIMENTAL PART

If we note (σ) generalized force corresponding to the surface (S), then the mechanical work (dW) required for modification iso-thermic surface area will be:

$$dW = - \sigma \cdot dS \qquad (1)$$

On the other hand this mechanical work is equal to the decrease of the surface free energy (dE, Gibbs energy change), so:

$$dE = \sigma \cdot dS \qquad (2)$$

$$\text{or} \qquad \sigma = \left(\frac{dE}{dS} \right)_{T,p,ni} [J / m^2] \qquad (3)$$

If we express mechanical work used to increase the surface (dS), as the acting force (dF) or displacement (d ℓ), then:

$$dW = dF \cdot d\ell = - dE = - \sigma \cdot dS \qquad (4)$$

This is another way of expression the surface tension, being force tangent to the surface, reported at length.

For a system being in energy balance, the free energy should be minimal. For a given volume which can have different values of the area, the lowest value being that of the spherical surface, because surface tension is constant, then the free energy will take different values, it will be minimal if the separation of the volume given will be minimal. This property explains why drops of liquid in a gas tend to form spherical, the surface having the smallest separation.

Pure liquids, composed of identical atoms or molecules, have generally a constant surface tension, which is established very quickly after the surface forming. For compound liquid, to reach equilibrium, it is necessary to pass a greater time interval.

Surface tension of a phase is defined as surface tension on the surface in the vacuum phase, while the surface tension of the interface phase in contact with those other phase voltage is inter-facial.

The inter-facial surface tension (σi), the limit of separation between a liquid and its vapour, in equilibrium is equal to the difference between the absolute surface tension liquid (σ ℓ) and its vapour (σv):

$$\sigma_i = \sigma_\ell - \sigma_v \qquad (5)$$

Knowing the values of (σi) and (σ ℓ) we could determine the absolute surface tension liquid (σv).

The same can be said in general, when we have two phases in equilibrium, the contact A and B (solid - liquid, solid - gas, liquid - gas, liquid - liquid, solid - solid, gas - gas);

$$\sigma_{i\,AB} = \sigma_A - \sigma_B \qquad (6)$$

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At critical vaporization temperature of the liquid $\sigma_i = 0$, because the separation surface has disappeared and so $\sigma_\ell = \sigma_v$.

In the case of two liquids in contact, the interfacial liquid - liquid tension will not be immediately determined, because the equilibrium between the two liquids will be set only after the two saturated solution will be formed. In the case liquid - gas system, the interfacial surface tension will be stabilized only when the gas dissolvation in liquid cease. The same phenomenon happens in the limit of separation between the crystals that is formed in the fusion.

The interfacial surface tension decreases with temperature, becoming zero at the critical temperature, when the separation surface disappears, like the relation of Eötvös shows:

$$\sigma_M = K_E\left(T_{cr}^{'} - T\right) \tag{7}$$

The equation is thus derived from the graphical representation of the variation of pure metals surface tension with temperature, figure 2, starting from the melting temperature (T_{top}) which corresponds the surface tension (σ_{Top}), we can write the equation of the right from the figure.

$$\sigma = \sigma_{top} - \alpha\left(T - T_{top}\right) \tag{8}$$

for $T = T'_{cr}$, $\sigma = 0$, so $\sigma_{top} - \alpha\left(T - T_{top}\right) = 0$ (9)

and substituting the σ_{top} the relation (9) in relation (10) we obtain:

$$\sigma = \alpha\left(T_{cr}^{'} - T\right) \tag{10}$$

Figure 2. Variation of σ with temperature T for pure metals

where α is the angle of right: $\alpha = -\dfrac{d\sigma}{dT}$; T - absolute temperature of the liquid; $T_{cr}^{'}$ - the critical absolute fluid temperature. Because $T_{cr}^{'}$ is constant for a pure metal, (σ) decreases with increasing temperature (T).

If we multiply the equation (10) with so-called "molar area" which is conventionally taken equal to $V^{2/3}$ (V being the molar volume of liquid) we obtain the free surface molar energy:

$$\sigma_M = \sigma \cdot V^{2/3} = \alpha\left(T_{cr}^{'} - T\right) \cdot V^{2/3} \sigma_M \tag{11}$$

and noting $k_E = \alpha \cdot V^{2/3}$ is obtained the relation (7). The constant (k_E) is the change of entropy for increasing the molar area ($V^{2/3}$).

Beginning from temperatures from 4 ... 7 degrees below the absolute critical temperature (T_{cr}) the surface tension varies no longer linearly with temperature. Besides temperature, the surface tension is influenced by other factors, including: the degree of dispersion, the nature of the phases, pressure, density decreasing and curvature radius of the surface.

The surface tension varies with the degree of dispersion and the specific surface of dispersed phase. Under specific surface we understand the relation between the surface phase and its volume. When the dispersion exceeds a certain limit, the surface tension starts to decrease, and when you reach the molecular dispersion of surface, the tension tends to zero. We find a large specific surface by porous bodies which have a great importance in the phenomena of filtration of liquids. The surface tension depends on the nature of the phases in contact, by their molar volume, polarity of molecules, the nature of links between the liquid particles, the phase's density. The surface solutions tension differs from that of pure metal in that the superficial layer has a different composition from the inner layers of the solution. The influence of pressure and radius curvature can be explained as follows: it is considered two fluids at mechanical balance, separated by an interface. The separation area between two fluids may take any form, from flat surface to the spherical. The condition of mechanical equilibrium at every point of the surface is given by Laplace equation.

$$\Delta P = P_2 - P_1 = \pm \sigma \cdot \left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{12}$$

Where: P_2 is the pressure from outside on the liquid; P_1- pressure inside the liquid, R_1 and R_2 are the radius of curvature in normal section, taken through the separation area. For spherical surface $R_1 = R_2$

$= R$ and $\Delta P = \pm \dfrac{\sigma}{R}$ (13)

For flat surface $R_1 - R_2 = \infty$ and $\Delta P = 0$.

If the two phases in equilibrium are separated by an interface curvature $C = \dfrac{1}{R_1} + \dfrac{1}{R_2}$, ΔP can be considered as the difference of pressure which push over interface from phase A (P_A) and from phase B (P_B)). Laplace's relation can be written as follows:

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$$P_A - P_B = \pm \sigma_i \cdot \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \tag{14}$$

where: σ_i is the interfacial surface tension. For spherical surfaces the relation (14) becomes:

$$P_A - P_B = \pm \frac{2\sigma_i}{R} \tag{15}$$

Besides the pressure difference (ΔP) determined by the surface curvature on each point of the surface separation of two phases, acts also the hydrostatic pressure. If in a particular point from the separation area is the pressure difference ΔP_O, at another point at height h, the pressure difference will be:

$$\Delta P_h = \Delta P_O + \gamma \cdot h = \Delta P_O + g \cdot h \, (\rho_A - \rho_B) \tag{16}$$

where: γ is the specific weight of the phase at a point; ρ_A and ρ_B - density of both phases A and B.

Entering the relation (16) and (14) is obtained:

$$\Delta P_h = P_A - P_B + g \cdot h \, (\rho_A - \rho_B) = \sigma_i \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \tag{17}$$

For linear system the surface tension can be expressed by the relation:

$$\sigma = \sigma_o - D(p - p_o) + (p - p_o)^2 \tag{18}$$

where: σ_o is the surface tension at pressure p_o; D - positive constant.
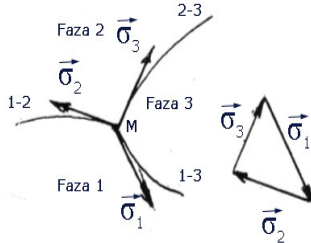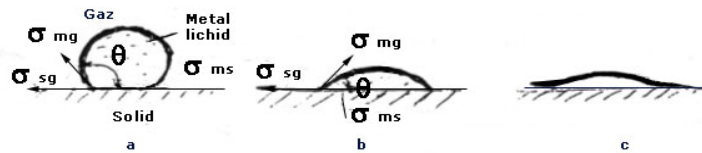

Figure 3. Way of action of inter-phasic tensions and of them composition

Figure 4. Shapes which could take the drop of metal liquid on the solid surface

According to equation (18) at pressures not too high, the surface tension decreases linearly with increasing pressure.

If we consider three crossing areas and which separate three phases, in a point of intersection (M), acts interfacial surface tension, figure 3.

At equilibrium must be satisfied the condition:

$$\sigma_1 + \sigma_2 + \sigma_3 = 0 \tag{19}$$

An important practice presents special phenomena of moistening the surface of solid melt. If we put a drop of metal melt on a solid surface, this may take the form shown in figure 4 a, b, c.

In the meeting of the three-phase surface tension acting σ_{sg}, σ_{mg}, σ_{ms} who must satisfied at equilibrium the Neumann's law relation (19).

The angle between σ_{mg} and σ_{ms} bears the name of moistening angle θ. At mechanical equilibrium must have therefore:

$$\sigma_{sg} - \sigma_{ms} - \sigma_{mg} \cdot \cos\theta = 0 \tag{20}$$

4. CONCLUSIONS

Moistening angle θ does not depend on the size fluid drop, but on the nature of the surface separation. As much the superficial tension of flow is lower, better the oxide film moistening and thus better protects the melt from the oven atmosphere, and the ability moistening flow from melt which need to be minimum at discharge the alloy from furnace to ensure the best possible separation of the melt flow during casting. Getting a solid particles moistening from fusion by flow is possible if the inter-phasic tension at separation limit between flow and nonmetallic inclusions is reduced. A good moistening of solid inclusions particles allow their easy removal of fusion. We have complete moistening when $\theta = 0$ and a "good" moistening when $\theta < 90°$; non moistening will occur when: $\sigma_{sg} > \sigma_{ms}$, $\cos\theta < 0$ și $\theta > 90°$; total moistening will be incomplete when $\theta = 180°$ and $\cos\theta = -1$.

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