Mathematical model of a stratification of metal melts in capillaries

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Abstract. The partial stratification of binary metal melts in crucibles during centrifuging, or in capillaries under influence of gravity, as yet has no consistent explanation within the framework of the existing theories of liquid state. The mathematical model of the stratification process based on assumed special properties of mononuclear skin (interphase layer) of a melt describing satisfactorily all experimental results on stratification of metals in capillaries is proposed.

The studying of metals stratification in crucibles under influence of centrifugal forces, and also in other cases, have been performed for almost 65 years, but their results till now have not a satisfactory theoretical explanation because of arising contradictions [1-11]. The main of them is that the calculated sedimentation rate of expected clusters having the $50 \times 10^{-10}$ m characteristic size is 7-8 orders less then the necessary for a quantitative explanation of experiment results. The existence of clusters of the necessary size (1000 times more) is contradictory to statistical thermodynamics, together with quantum mechanics, which are not able to explain existence of two various stable bonding types between metal atoms in clusters and in surrounding them amorphous melt, which are under the same conditions.

The most extensive experiments on “clusters sedimentations” have been performed by one of the authors of the present work [9, 10]. In these works the process of segregation of metal melts by gravity in vertical alumina or silica capillaries of diameter 0.3–3 mm and length 40–500 mm was studied. The duration of the experiment was 5 to 240 min.

It was noticed that appreciable liqation of alloy components over the length of samples had occurred only for those of them which in liquid state were held in vertical position, while the process of such redistribution of components was rather slow, and the achieved distribution tends to an equilibrium with time. The degree of attained inhomogeneity also depended on alloy composition, on its temperature in liquid state and on sample height. As the sample height is increased the degree of attained heterogeneity tends to considerable growth, but the time of achieving the equilibrium seemed to increase considerably. Authors of [10] found the stratification effect for alloys having phase diagrams of a various types.

Review of the experimental data of works [9,10], including for comparison the results of the predecessors, do not leave doubts that the distribution of melt components on height of capillaries is just connected with a gravitational field, and also, with ratio of a vertical interphase to a melt volume, depended, first of all, with a capillary diameter. It obviously indicates a key role of last
parameter for stratification process, or, in other words, that the process proceeds just in surface layer of a melt.

In [11] some factors affecting the mass transfer in molten metals were reviewed, and another mechanism of a partial stratification of metal melts in crucibles or capillaries was proposed. The Inertial Surface Separation (ISS) effect consisting in spontaneous concentrating (adsorption) of one component of surface layer due to a smaller surface energy [12], with the subsequent flow of this layer, separated by density from other melt, on a capillary wall upwards or downwards at the expense of hydrostatic equilibrium violation, was supposed to take place. Later [13] some discrepancies of this mechanism were also discovered with actual experimental data when the concentration of adsorbed component in surface melt layer is insufficient for an explanation of experiment results.

The concentration of a surface-active substance in surface layer can be calculated from the Gibbs's equation:

$$\Gamma \approx -\frac{c}{R \cdot T} \frac{d\sigma}{dc} \tag{1}$$

where $\Gamma$ is an excessive number of component moles in surface layer volume compared with its volume concentration.

Table 1 lists the ratios of surface energies and densities of pair components, and absolute differences of these values for binary metal systems [14], explored in [9,10].

Let's consider, as an example, an alloy of Sn with Pb containing 40 % (mass) of Pb. The surface energy of this system was explored more than once. According to [15], deviations from additive for this property of alloys are insignificant, and, hence, the influence of composition on a surface energy can be without a major error approximated with a linear relation. For the above-mentioned alloy with 27.65 % (molar) of Pb, the value of a partial derivative of equation (13) is $-0.8410^{-3}$ J/m$^2$ · (%), and for lead the quantity of adsorption is $\Gamma = 4.9 \times 10^{-6}$ mole/m$^2$.

Table 1. Relation of a surface energy and density of molten metals included in investigated binary melts.

| Melt components A | B      | $\sigma_A/\sigma_B$ | $\sigma_A-\sigma_B$ | $\gamma_A/\gamma_B$ | $\gamma_A-\gamma_B$ | Temperature of comparison, °C |
|-------------------|--------|---------------------|---------------------|----------------------|----------------------|-----------------------------|
| Tin               | Lead   | 1,17                | +83                 | 0,658                | -3,61                | 300                         |
| Bismuth           | Cadmium| 0,7                 | -167                | 1,25                 | +2,0                 | 250                         |
| Aluminium         | Silicon| 0,77                | -271                | 0,94                 | -0,15(!!)            | 800                         |
| Lead              | Bismuth| 1,26                | +101                | 1,058(!!)            | +0,58                | 300                         |
| Zinc              | Aluminium| 0,855             | -274                | 2,77                 | +4,2                 | 425                         |
| Bismuth           | Antimony| 0,94               | -24(!!)             | 1,051(!!)            | +0,49                | 500                         |
| Copper            | Tin    | 2,64                | +848                | 1,146                | +1,02                | 1000                        |
| Copper            | Lead   | 4,47                | +1060               | 0,755                | -2,59                | 1000                        |

If assume the thickness of surface layer $\delta = 1 \times 10^{-6}$ m., then about 5 g-mole of Pb will be added into 1 m$^3$ of such solution due to adsorption. Density of alloys also is close to additive, therefore, if density of original melt can be evaluated as 8069.58 kg/m$^3$, then density of surface layer will be 8069.93 kg/m$^3$, that is 0.35 kg/m$^3$ (0.0043 %) more.

So, the increase of Pb concentration in surface layer is three-orders lower than quantity of attainable enrichment of melt in capillaries in their bottom part. Judging from this, the experiment data cannot be explained. The accordance with them could be improved if the thickness of adsorbed layer is supposed three orders less, however in this case an insuperable contradiction arises which related with equilibrium character of an achieved stratification. If assume that the adsorptive layer is flowing, the process will proceed practically to a complete stratification of components for two beds.

As the restrictor of a stratification can serve only the slow back diffusion, which productivity decreases with reduction of a diameter and, correspondingly, capillary cross section, and at the same time, as was indicated earlier, the decrease of a capillary diameter accelerates stratification.
Thus, that the assumption of adsorbed layer flow stated by one of authors earlier in [11] has evidently failed. However, the conclusion concerning flow of exactly near-surface layer remains invariable.

It is clear also that Pb flows downwards, and more Sn flows upwards, and this follows from asymmetry of the experimental curves [9, 10] (figures 7 and 8) - it can be seen that when the process was already steady (lower curve) in top part of a capillary, in its bottom the lead is still flowing from upper layers of a melt (the upper curve). The rate of concentration change also allows to believe that it is pure metal that flows. For example, for pure Pb, it follows from the mass balance that at its normal viscosity the thickness of flowing layer is 7000 atoms. It is impossible to explain the formation of such film; besides, in some experiments the temperature was below Pb melting point.

Only melt monoatomic layer adjacent to a capillary wall is under the special conditions. In connection with above-stated, the most reliable assumption is that precisely this layer is responsible for a stratification process. From such point of view, it is necessary to admit that, in this case, atoms of Pb and Sn should move independently over interphase actually as a continuous film at an extremely high speed. It is an only way to get over all the contradictions shown above.

The travelling speed of Pb atoms calculated from a material balance at film thickness of one atom is tens cm/s (up to 0.3 m/s [11]), that corresponds in order to velocity of metal-on-metal flowing, or a surface-active substance flowing on a water surface, and, consequently, it seems plausible. (Calculated speed of a Pb monoatomic film from hydrodynamical equations at melt normal viscosity is $10^{-12}$ m/s).

Such flowing is possible in case the metal atoms or molecules which are in interphase layer, practically do not interact with a material of a crucible and atoms of inter layer metal, representing something like two-dimensional gas (non-ideal Bose-gas). These results are interpreted in works [13,16] as high-temperature super fluidity. According to this hypothesis, the capillary stratification, apparently, has the following mechanism (for an example of tin - lead melts).

The heavy atoms of Pb flow downwards over interphase, and the atoms of Sn are displaced upward over the film, then they diffuse into volume of a sample and change its composition.

In this case, in connection with change of local volume of substance in the lower and upper parts of a sample, an equalizing melt flow over the sample is formed. As a result, the composition of its bottom part is enriched with lead, and this is observed in experiment. Thus the most difficulty is to explain why flow stops at any equilibrium value of a concentration difference between top and bottom of a sample, that was observed earlier [9,10,13]. In our opinion, the sole cause of this equilibrium concentration difference in a system of different density particles having practically unlimited mobility over interphase boundary (similar to molecules of 2-dimensional gas), is their barometric distribution under Archimedes forces arising in a field of gravity, or field of centrifugal forces applied to a system. According to [17] concentration of a heavy component (molecular ratio) can be calculated from the following expression:

$$C_{arch} = C_{arch0} \cdot \exp\left(-\frac{h \cdot g \cdot \left(\mu_1 - \frac{\mu_2 \cdot V_{s1}}{V_{s2}}\right)}{T}\right), \quad (2)$$

where $C_{arch0}$ is the concentration of a heavy component at mix height $h$, equal to zero; $\mu_1$ and $\mu_2$ – are molecular weights of both components; $V_{s1}$ and $V_{s2}$ are molar volumes of atoms in interphase (surface) layer.

When groups of same atoms in a 2-dimensional state with $\alpha_1$ and $\alpha_2$ association ratio are formed, molecular weights and the volumes of these metamolecules (clusters) as a first approximation can be found from expressions:

$$M_1 = \alpha_1 \cdot \mu_1; \quad M_2 = \alpha_2 \cdot \mu_2; \quad V_{s1} = \alpha_1 \cdot V_{s1}; \quad V_{s2} = \alpha_2 \cdot V_{s2} \quad (3)$$

In view of this circumstance, and, considering, that all interphase layer, being initially chemically equilibrium with a 3-dimensional melt, is redistributed according to expression (2), it is possible to calculate value $C_{arch0}$, designated further as $C_{okl}$:
\[ C_{kl} = \frac{\alpha_1 \cdot C_{klo} \cdot \beta}{T \left[ 1 - \exp \left( -\frac{\alpha_1 \cdot \beta}{T} \right) \right]} , \]  
\[ (4) \]

where \( C_{klo} = \frac{\alpha_2 \cdot ce}{\alpha_2 \cdot ce + \alpha_1 \cdot (1 - ce)} \), and \( \beta = g \cdot H \cdot \left( \mu_1 - \frac{\mu_2 \cdot vs1}{vs2} \right) \).

In expressions (4) \( ce \) is average molar fraction of a heavy component in an original sample; \( H \) is full height of allocation (height of a melt in a vertical capillary).

Concentration \( C_{kl_i} \) of heavy metamolecules at height \( h_i \) is described, correspondingly by an equation similar to equation (2):

\[ C_{kl_i} = C_{klo} \cdot \exp \left( -\frac{g \cdot h_i}{T} \cdot \left( M1 - \frac{M2 \cdot VS1}{VS2} \right) \right) , \]
\[ (5) \]

and, eventually, the concentration of a starting heavy component \( 1 \) for \( i \)-height will be equal to

\[ c_{ls_i} = \frac{\alpha_1 \cdot C_{kl_i}}{\alpha_1 \cdot C_{kl_i} + \alpha_2 \cdot (1 - C_{kl_i})} \]
\[ (6) \]

Essential factor determining the logic of the further reasoning’s, is the time of equilibrium achievement at similar segregation.

The characteristic time of precipitation (fall) of atom having a greater density from height \( H \), which corresponds, on the average, to concentration 50 \% (vol.), in view of Archimedes forces and at viscosity lack (ideal fluid) can be evaluated by:

\[ \theta = 2 \cdot \frac{H \cdot \rho_1}{g \cdot (\rho_1 - \rho_2)} \],
\[ (7) \]

For Sn - Pb system in a sample 1 m high the precipitation time is slightly more than 1 s. For a sample 0.22 m high, it is less than 0.6 s (average travelling speed is 0.45 m/s.). Improved calculations from an equation of body motion in a theoretical super fluid liquid result in approximately twice smaller estimation of fall duration.

So, by experimental results [9, 10], the limiting factor of the process is the diffusion of components from inside to a surface of a sample, therefore the process is extended for minutes and hours. The incommensurability of these two values allows to simplify a calculation procedure of molten metals capillary segregation, assuming that it always proceeds in conditions of practically equilibrium distributions of components on height of interphase layer.

It is valid especially at the end of the process, when the diffusion is retarded because of reduction of concentration differences between a sample and super fluid film.

In this case the quantity of the transferred heavy component \( \Delta n_{1_i} \) in the bottom part of a capillary from a two-dimensional film phase \( s \) into a phase of a three-dimensional sample \( f \), as a first approximation, is proportional to a difference of concentrations, value of a transfer surface, transfer duration \( \Delta \tau \) and transfer coefficient \( Y \):

\[ \Delta n_{1_i} = (c_{ls_i} - c_{f_i}) \cdot 2 \cdot \pi \cdot r \cdot \frac{H}{N} \cdot Y \cdot \Delta \tau , \]
\[ (8) \]

where \( r \) is capillary radius; \( N \) is number of elementary cells over sample height \( H \), when all sample is considered. The value of a counter flow of the second component is linearly dependent of quantity of the first component, and it can be calculated on the basis of the continuity equation transformed for the given case. It is suggested that the area of a two-dimensional film should remain constant. In this connection it is possible to write down a ratio:
It is evident, that when a composition of i-cell of a sample is changed, a volume defect arises which can be calculated using expression:

\[ \text{def}_i = v1 \cdot \Delta n_{1_i} + v2 \cdot \Delta n_{2_i} \]  

(9)

\( v1 \) and \( v2 \) - mole volumes of components in a phase of a sample \( f \). For any i elementary calculating cell the complete volume defect is the sum of defects of all previous cells:

\[ \text{Def}_i = \sum_{1}^{i} \text{def}_j \]  

(10)

In this case for each cycle \( \Delta t \) of calculation the concentration of a heavy component in every i-cell will change and become equal:

\[ cA_{f_i} = \frac{A_{1_i}}{A_{1_i} + A_{2_i}} \]  

(11)

where:

\[ A_{1_i} = m1_i + \Delta n_{1_i} - m1_i \cdot \frac{N}{\pi \cdot r^2 \cdot H} \cdot \text{Def}_{i} + m1_i \cdot \frac{N}{\pi \cdot r^2 \cdot H} \cdot \text{Def}_{i-1} \]  

\[ A_{2_i} = m2_i + \Delta n_{2_i} - m2_i \cdot \frac{N}{\pi \cdot r^2 \cdot H} \cdot \text{Def}_{i} + m2_i \cdot \frac{N}{\pi \cdot r^2 \cdot H} \cdot \text{Def}_{i-1} \]  

Here \( m1_i \) and \( m2_i \) are quantities of moles of components in i-cell before the beginning of each cycle. The values of coefficients of transfer are defined by selection from a condition of the best conformity to results of dynamic experiments. At the same time they relatively slightly effect a character of equilibrium distribution, as the calculated data approach asymptotically to experimental, and when process duration is more than 2 hours, they change then insignificantly.

The complete description of experimental data obtained in works [10,11] is given further. Figure 1 shows the design curve of Pb concentration distribution over the height of a sample calculated for coefficients of association, \( \alpha 1 \) and \( \alpha 2 \) are equal to 1 in comparison with experimental data of figure 2. The exact quantitative agreement can be observed when \( \alpha 1 \) and \( \alpha 2 \) equal to two (figure 3). In our opinion, this does not contradict to the data on metal properties. In particular, it is known that the metals are partially dimerized even in vapor condition. Therefore all further computations, except for special cases, were conducted for association coefficients equal to two.

The curves notation in figures is as follows: a symbol “T” refers to theoretical computation; the numbers designate composition, temperature, diameter and length of a capillary, respectively. Symbols “V” and “N” refer to a top and a bottom of a sample, respectively; “Y” stands for calculated. Sign “C” refers to Pb.

Figures 1-9 present the experimental data for a system Sn-Pb and calculated relations obtained when the experimental conditions (partially reflected in curve descriptions and presented in table 2) were introduced to the initial equations.

Inverse relation of transfer coefficient from process temperature has been revealed for tin-lead system: the less is a temperature, the more is a coefficient (figure 4). As noted above the transfer coefficient depends on diffusion coefficient, which in its turn directly depends on temperature. So the obtained result needs to be explained. In our opinion this may be explained by the fact that, according to expression (5), at low temperatures the achieved equilibrium concentration difference over a capillary height is more than at high temperatures. So, the driving force of the process (concentration
difference in expression (8)) at high temperatures decreases, and when this factor outstrips a diffusion growth, it results in reduction of intensity of transfer.

Figure 4 shows the dependence of the log \( \log(Y) \) on inverse temperature which has allowed a formal activation energy for the process to be calculated. It has appeared equal to 5400 Cal/mole, that satisfactorily corresponds to self-diffusion activation energy for Sn and Pb, 4570 and 4450 Cal/mole, respectively [14].

Figure 5 represents the comparison of achieved in experiment within one hour and theoretically calculated (designated \( \log(Y) \)) differences of Pb concentration at the ends of capillary 0.22 m in length.

Figure 6 shows the comparison of lead distribution over capillary height for eutectic alloy when overheat temperature is 50°C more than eutectic temperature (\( c_i \) is theoretical distribution from expression (5); \( w_i \) is computation at \( \log(Y) - 4 \times 10^{-3} \) (from figure 4); C38506, experiment).

Figures 7-10 show an alloy stratification under various experiment conditions (table 2). Figure10 shows data for an Cu - Sn alloy.

**Table 2. Parameters of experiments** [9, 10] **for tin - lead, tin - copper and zinc - aluminum systems**

| Figure number | Pb (Cu, Zn) content, mass fraction | Temperature T, K | Capillary height, H, m. | Capillary diameter, d·10^{-3} m. | Time of experiment, min. | \( \alpha_1 \) | \( \alpha_2 \) | VS1/VS2 |
|---------------|-----------------------------------|------------------|-------------------------|-----------------------------|----------------------|-----------|-----------|---------|
| 1 calculated  | 0.4                               | 473              | 0.22                    | 1                           | 60                   | 1         | 1         | 40/34   |
| 2             | 0.4                               | 473              | 0.22                    | 1                           | 60                   | 2         | 2         | 40/34   |
| 3 calculated  | 0.4                               | 473              | 0.22                    | 1                           | 60                   | 2         | 2         | 40/34   |
| 5             | 0.4                               | 473              | 0.20                    | 1                           | 180                  | 2         | 2         | 40/34   |
| 6             | 0.38                              | 506              | 0.22                    | 1                           | 60                   | 2         | 2         | 40/34   |
| 7             | 0.38                              | 506              | 0.05                    | 1                           | 90                   | 2         | 2         | 40/34   |
| 8             | 0.38                              | 506              | 0.22                    | 1                           | 90                   | 2         | 2         | 40/34   |
| 9             | 0.39                              | 506              | 0.22                    | 1                           | 180                  | 2         | 2         | 40/34   |
| 10 Cu         | 0.91                              | 1323             | 0.06                    | 2.5                         | 240                  | 2         | 2         | 16/34   |
| 13 Zn         | 0.98                              | 698              | 0.1                     | 0.8                         | 180                  | 2         | 2         | 16.9/23 |

The most unusual and interesting results of works [9, 10] are the data on a stratification in a capillary of eutectic Al-Si alloy overheated by 50°C above a liquidus line. Density of Si in a liquid state is higher, than density of Al, but it concentrates in the top of a capillary. According to the equation (5) it is possible only for a positive value of exponent argument. At a reasonable ratio \( VS1/VS2 = 1.35 \) the best compliance of the experimental and calculated data is in case \( \alpha_1=30 \) (Si), and \( \alpha_2=2 \) (Al).

Reduction of the volume ratio results in unreasonably large values of \( \alpha_1 \) coefficient. Taking into account a nature of Si, the proposed value of its association coefficient is also considered acceptable (figure 11, \( c_i \) - theoretical distribution over capillary height \( h \), see equation (6); \( w_i \) - calculated; y - experiment; a capillary diameter is 1 mm.). Deviation of the theory from experiment most likely is related with the fact the actual Si content in the experiment was a little higher than eutectic.

The effect of the element inherent properties on \( \alpha_1 \) is also true in a case of Bi, for which the least deviation from experimental data is observed at \( \alpha_1=4, \alpha_2=2 \) (figure 12), Bi604671Ti is for
calculation; HBi604671i; - height (length) of a capillary. Temperature: 467K, capillary diameter: 1 mm; the initial bismuth content: 60% mass, cadmium: 40%).

Table 3 shows the comparison of the calculated and experimental results for 180 min stratification of Al - Si alloys in a capillary with a 2 mm diameter, 90 mm height, at 50°C higher then liquidus line, depending on initial composition of a sample.

Figure 13 represents data on a stratification of 96 % Zn - Al melt. The conditions of experiment are given in table 2.

| Initial concentration of silicon, % (mass) | 6  | 7  | 8  | 9  | 11 | 12 | 13 | 14 |
|------------------------------------------|----|----|----|----|----|----|----|----|
| \( \Delta C_{\text{exp}} \)             | 0.8| 0.9| 1.08| 1.8| 1.87| 2.08| 1.8| 1.98|
| \( \Delta C_{\text{calc}} \)            | 1.21| 1.41| 1.61| 1.8| 1.99| 2.32| 2.49| 2.64|

**Conclusions**

The proposed mathematical model satisfactorily describes experimental data and has forecasting force as concerning equilibrium and dynamics of metal melt stratification within the accuracy of mass transfer coefficient.

The phenomenon of a melt stratification in capillaries can be applied in mixed metals separation and/or when manufacturing the castings with a coordinate gradient of concentration, to study physical and chemical properties of liquids, and also in other fields of a science and technology.
Figure 13

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