Synthesis of compounds of impurities with chemically active additives in liquid aluminum and gallium

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Abstract The method of binding of impurities in liquid metal by means of formation of intermetallic compounds (IMC) with the active additives has been developed to improve the quality of nonferrous metals. The special technological process promotes the growth of IMC microcrystals and separation of suspensions. The probability of impurity removal from draft metal is estimated on the basis of Delimarsky and Karapetjants formulas. Purification of gallium was carried out by introduction of approximately 1 % of sodium or lithium. Results of calculation and experiment are in good agreement. Efficiency of purification from impurities increases in a sequence Zn<Sn<Pb<Bi. Removal of silicon from liquid aluminum by separation of IMC with grafitized fabrics has allowed to arrange additives of active metal by efficiency of removal in a sequence Mg<Ca<Sr and Sc<Y<Ba.

The 1/5 part of world production of aluminum is applied for various kinds of a foil for packing and only 1/50 part for aircraft construction, so this metal instead of "winged" has become now "packing". The manufacturing of nonferrous metals from a scrap metal is far more cheap, than from the raw material. In particular, aluminum meets rigid requirements on containing such impurities as sodium, silicon, iron, copper, zinc, etc. The residual concentration of intermetallic compounds (IMC), and the size of these particles play the key role in some aspects, such as regeneration of aluminum gallam in a manufacture of hydrogen (developed at Purdue University), application of aluminum gallam in an extraction of gallium from the solutions of alumina production (introduced by our Institute at plants in Russia and China), and application of light, strong, corrosion-proof, and weldable aluminum alloys on transport and in construction (developed in Russia by a number of Institutes).

For many years we are developing the methods of purification from impurities due to their binding in liquid metal by IMC formation with the active additives, growth of microcrystals of these compounds and separation of a formed suspension [1]. The estimation of a possibility of removal of an impurity from draft metal by synthesis of compounds of an impurity with chemically active additive in liquid-metal medium is carried out on the basis of known regulations of chemical thermodynamics.

Comparison of enthalpies of formations (∆H) and temperatures of fusion (T) formed with impurity IMC in comparison with corresponding values for compounds of active metal with base metal allows to estimate relative durability (RD) of formed compound of impurity under the formula proposed by Delimarsky [2]:

$$RD = \frac{\Delta H_1 - \Delta H_2}{\Delta H_2} \cdot \frac{T_1 - T_2}{T_2}.$$
Using this formula, it is possible to choose the active metal forming the most stable compound with impurity. Another way of a choice of suitable active metal is the method of comparison of increments of standard entropies of IMC formation in a crystal state $I_{298}^0$ in a series of similar compounds according to Karapetjants [3]:

$$\Delta E = E_{12} - E_{32} = (I_{1}^0 - I_{2}^0) - (I_{3}^0 - I_{2}^0) .$$ (2)

Indexes 1, 2 and 3 refer to metal impurity, active metal of the additive and base metal, respectively.

Purification of gallium was carried out by introduction of about 1% of sodium or lithium with heating up to 800°C in an inert atmosphere. After slow cooling for IMC crystallization the melt was filtered through the porous glass filter (diameter of pores is about 40 microns) at temperature near to that of gallium fusion (30°C) on air. Unbounded active metal together with IMC in the form of oxide film remained on the filter. As a result (table 1) the metal has been refined tens times from impurities of tin, lead and bismuth, and several times from zinc. Such characteristics as relative durability and difference of entropy increments confirm qualitatively the increase of purification efficiency in a sequence of impurity Zn < Sn, Pb < Bi in gallium.

Table 1. The relative durability (RD), differences of entropy increments IMC (ΔE) and efficiency of Ga purification by active metals Li and Na.

| Impurity | RD$_{Li}$ | ΔE$_{Li}$ | RD$_{Na}$ | ΔE$_{Na}$ |
|----------|----------|----------|----------|----------|
|          |          |          |          |          |
| Zn       | –        | 0.2      | 0.01     | 0.2      | 0.012   | 0.004   | 3–6     |
| Sn       | 0.08     | 3.8      | 0.05     | 3.8      | 0.110   | 0.003   | 30–50   |
| Pb       | –        | 7.3      | 0.20     | 7.3      | 0.025   | 0.0012  | 20–50   |
| Bi       | 1.35     | 7.9      | 1.10     | 7.9      | 0.045   | 0.00088 | 50–80   |

Mechanical removal of an impurity is an efficient process if the impurity in melt is in the form of fairly large particles. For example, it is known that upon centrifugation of liquid aluminum with the speeds up to 2500 rpm the finest particles of aluminum carbide Al$_4$C$_3$ have the size of 2 microns. For heavier inclusions, the diameter of particles can be calculated using the Stokes equation and it should be larger than 0.5 microns [4].

The study of solubility of many metals in gallium by saturation and the following filtration of the melt through a porous filter showed that their solubility up to several at.% is described by the equation

$$\lg C = A - B/T .$$ (3)

This formula agrees with the thermodynamic expression for equilibrium between solid and liquid phases deduced from equal activity of dissolved and solid components relative to same chosen standard state and also from some other simplifications. However for very small values of solubility at temperatures close to gallium fusion temperature, calculated and experimental values of solubility do not agree (table 2).

For well soluble metals having high concentrations in gallium, coarsening of IMC occurs easier and more quickly. For poorly soluble TiGa$_3$, the divergence of results is the greatest, whereas for the most soluble CuGa$_4$ (stable below 527 K) it is within the limits of an analytical error. Centrifugation of suspensions (at the speed of 2500 rpm) makes it possible, at least for nickel, to approach the data obtained by extrapolation of solubility of NiGa$_3$ at higher temperatures. Nanodimensional particles are found in the melt at greater speeds of cooling (100–1000 K·s$^{-1}$) for Al–Sc alloys [5]. The formation of nanocrystalline structures in Al-Mg-Sc alloys due to intensive plastic deformation is reported in [6].
Table 2. Experimental and calculated from equation (3) values of solubility of Ti, Ni and Cu in gallium at 303 K, at.%

| Metal | Coefficient  | Calculated values | Experimental before filtration | upon centrifugation |
|-------|--------------|-------------------|-------------------------------|---------------------|
|       | A           | \(-B\), \(10^3\) |                               |                     |
| Ti    | 2.60        | 3.12              | \(2.00\times10^{-8}\)         | \(1.8\times10^{-3}\) | \(4.4\times10^{-4}\) |
| Ni    | 2.52        | 1.85              | \(3.85\times10^{-4}\)         | \(9.8\times10^{-4}\) | \(4.4\times10^{-4}\) |
| Cu    | 3.52        | 1.61              | \(1.6\times10^{-2}\)          | \(1.8\times10^{-2}\) | \(1.6\times10^{-2}\) |

Aluminum was purified from silicon by silicon binding in IMC on graphitized materials made of fabric and felt with a special filtering layer made of the corresponding IMC. The amount of active metal for interaction with an impurity should be sufficient for formation of the most stable IMC with a surplus to set off losses. The active additive was in the form of about 10% master-alloy. In liquid aluminum, a tablet of the master-alloy was added under an argon bell. Primary aluminum contained 0.040 to 0.180 wt.% of silicon. Alkaline-earth metals, scandium, yttrium and zirconium were tested as active metals of the additive. It was found that upon removing IMC by filtration the content of silicon in liquid aluminum decreased in the sequence from magnesium to barium and from scandium to yttrium (table 3).

Table 3. Removal of silicon from liquid aluminum as a result of IMC separation by filtering.

| Sample                      | Active additive |
|-----------------------------|-----------------|
|                             | Mg  | Ca  | Sr  | Ba  | Sc  | Y   |
| Primary Al                  | 89  | 86  | 86  | 84  | 87  | 180 |
| Upon separation of IMC      | 87  | 81  | 80  | 66  | 81  | 150 |
| Decrease of Si content      | 2.3 | 5.8 | 6.9 | 21.4| 6.9 | 16.7|

Sometimes the IMC formed in the reaction with the active metal of the additive need not be removed from the liquid aluminum. To improve the quality of the conducting aluminum alloy A5E (Al 99.5 %, Fe 0.18–0.35 %, Si 0.12 %, Cu 0.02 %, Zn 0.04 %, etc. 0.03 %) it is sufficient to decrease the content of silicon in the solid solution and convert it in the corresponding IMC. Silicon as an impurity in the solid solution makes the main contribution to an increase of electric resistivity. Addition of calcium suppresses the effect of silicon on resistivity of technical aluminum. In the Al–Ca–Si system, there is quasibinary section going through aluminum and the CaSi2Al2 compound [7]. We found that addition of a dosed amount of calcium appreciably decreased the resistivity even when the content of silicon is below 0.10 wt.% (figure 1). For conducting aluminum A5E and A7E, an enhanced mechanical durability is of importance, but cannot be provided by small addition of calcium (figure 2). According to the quasibinary cross-sections of phase diagram the aluminum alloys have improved strength and electric conductive characteristics [7, 8]. The tensile strength of hard-drawn and annealed samples of the base conducting aluminum (BCA) alloy A5E with addition of scandium, zirconium, yttrium and calcium was measured. For annealed samples of Zr_an, Sc_an, Y_an with the considered additives, resistivity \(\Delta \rho = (\rho_{\text{ad}} - \rho_{\text{base}})/\rho_{\text{base}}\) increases almost linearly, while for a calcium additive in BCA, resistivity decreases when its content is 1% (figure 1). The enhancement of mechanical properties \(\Delta \sigma = \sigma_{\text{ad}} - \sigma_{\text{base}}\) in absolute values (MPa) for annealed samples is maximum for yttrium and minimum for calcium (figure 2). For hard-drawn samples, both resistivity and tensile strength are essentially higher.
Figure 1. Increase of resistivity (Δρ, %) of annealed samples of base conducting aluminum, alloyed (wt.%) with zirconium, scandium, yttrium and calcium at 20°C.

Figure 2. Tensile strength (Δσ, MPa) of hard-drawn (hd) and annealed (an) samples of the A5E alloy with of scandium, zirconium, yttrium and calcium additives.
Figure 3. Resistivity of aluminum alloy versus the content of silicon and calcium (x is Ca content, wt. %, y is Si content, wt.%, z is resistivity, Ohm-mm²/m). Recommended structure is given in the text.

Figure 4. Durability of aluminum alloy versus the content of silicon and yttrium (x is Y content, wt.%, y is Si content, wt.%, z is durability, MPa).

The content of silicon in BCA can vary widely, therefore the data on resistivity and durability of aluminum alloys are given in figures 3 and 4 in the form of the corresponding surfaces as functions of the content of calcium, silicon and yttrium, silicon.

Average values obtained in some tests on simultaneous doping of BCA with calcium and yttrium show that resistivity of conducting aluminum can decrease by about 1 % and durability can increase
by 16% or at the same resistivity the durability of wire can increase by 34% (the respective structures are indicated by arrows on figures 3 and 4).

The results of intermetallic purification of such liquid metals as aluminum and gallium for the improvement of the quality of secondary metals are discussed by the same authors in another paper of present proceedings. New fabrics and felts stable to aggressive liquid metals, which appeared recently, considerably expand the usability of filtration purification of melts. For example, the fabric made of thin strings of boron nitride withstands temperatures to 2400°C. This fabric having a special frame may be used for filtering for many months without being replaced. The method of intermetallic purification from impurities is more environment friendly and requires no complicated equipment used in such methods as rotor degassing, purification in flowing or submersible centrifuges. The proposed methods can be efficiently applied to purification of secondary metals and primary aluminum, as well as to solve some other problems of improvement of the metals quality.

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