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Received on 07.12.2007

UDC 669.871.5

PHASE REVERSAL ORGANIZATION IN GALLIUM-EXCHANGE SYSTEMS

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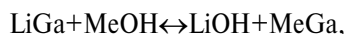
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Phase reversal stages at alkalis separation by chemical exchange method in LiGa-NaOH and LiGa-KOH systems have been studied. Pilot laboratory plants for intermittent and continuous obtaining lithium gallium in metal melts were developed and tested. The possibility of realization of alkalis multiple separation process by gallium-exchange method in packed column was shown.

Introduction

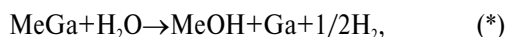
One of perspective substance segregation and purification techniques is chemical exchange method as it does not require energy consumptions for direct segregation process. The gas-liquid system is the most manufacturable of all systems for element segregation by this method. However, many elements of Periodical system, in particular, a number of alkalis have no gaseous compounds [1]. These elements may be segregated by the chemical exchange method using liquid-liquid system. Water solution of alkaline element salt is one liquid as a rule and amalgam is used as the second one. Amalgam-exchange segregation method has a significant disadvantage as it uses high-toxic mercury in large quantities. We proposed to change high-toxic amalgams used in processes of exchange segregation and purification of alkali metals for environmentally safe compounds of gallium with alkalis – gallamas [2].

Segregating alkalis (Li, Na, K) by gallam-exchange method the exchange reaction



occurs in gallama system lithium-water solution of sodium hydroxide (potassium), where Me is sodium or potassium.

Simultaneously with the given exchange reaction the intermetallic compound (gallama) is decomposed by the reaction



in this case alkali transfers into solution. If decay rate of gallama is higher or equal to the rate of elemental

exchange in the given system then it is impossible to separate alkalis in it. Therefore, the kinetics of the given processes in the systems LiGa-NaOH and LiGa-KOH in temperature range 40...80 °C were studied [3]. It was stated that the rate of exchange process exceeds the rate of gallama decomposition process approximately in 40...70 times in the studied temperature range. So, it is arguable that manifold multiplication of single separation effect is possible in these systems.

For implementation of multiple separation process of alkalis by gallama-exchange method in packed columns the questions of organizing counterflow and reversal of exchanging phases are required to be considered. The possibility of organizing phase counterflow and conditions necessary for this are showed in the paper [4]. The given article is devoted to the study of organization of exchanging phase reversal in the systems Li-Ga-NaOH and LiGa-KOH.

The process of phase reversal includes two stages of metal conversion: 1) from gallama phase into hydroxide solution – gallama decomposition; 2) from hydroxide solution into gallama – gallama obtaining.

First of all, as it was said above, the kinetics of alkali gallama decomposition process was studied. It was stated that gallama is well decayed with water by the reaction (*), and the rate of its decomposition is about two times higher than the rate of amalgam decomposition in similar conditions. Besides, it is possible to increase the rate of the given process behavior with the help of catalysts (for example, graphite). Thus, the first stage of phase reversal is easily implemented.

Lithium gallama may be obtained in two ways: electrochemical – electrolysis of electrolytes in aqueous and nonaqueous solutions and alkali direct dissolution in gallium (in metal melts).

Electrochemical obtaining of lithium gallama

Let us briefly consider the results of investigations on obtaining lithium gallama by electrochemical method.

The experiments in obtaining lithium gallama by electrolysis with gallium cathode from electrolyte aqueous solutions were carried out in this direction. The conclusion made by the results of the given investigations coincides with authors' conclusion [5]: low hydrogen overstress on gallium results in the fact that hydrogen ion transfer reduces lithium ions transfer almost to zero that makes impossible using the given method for obtaining lithium gallama. To decrease electric transfer of hydrogen ions the cationite and anion membranes by which electrodes were isolated were used. Maximal current output of lithium was not higher than 50 %.

The attempt to use water-organic solvents (water-ethanol) was not successful as well. Even insignificant presence of water (4 %) in electrolyte solution decreased considerably the value of current output of lithium (up to 30 %). Therefore, it is reasonable to use nonaqueous (organic) solutions of electrolytes for obtaining lithium gallama.

Experiments in obtaining lithium gallama by electrolysis with gallium cathode from nonaqueous solutions of lithium chloride in propylene carbonate carried out by the authors [6] showed that this method of obtaining lithium gallama has almost 100 % of current output of lithium and suitable for organizing phase reversal. However, at its using the difficulties with the conversion of aqueous solution of lithium hydroxide into organic one occurs as lithium hydroxide is not directly solved in organic solvents. Therefore, it should be firstly converted into a certain intermediate chemical form (for example, lithium chloride) and then the organic solution of this compound is obtained and from this solution the lithium gallama is obtained by electrolysis. Besides, the purification of the obtained lithium gallama from organic solvent traces is required for its further use in segregation process.

Owing to specified difficulties use of the given method for obtaining lithium gallama is undesirable at phase reversal in the researched exchange systems.

Obtaining lithium gallama by direct dissolution of lithium in gallium

Lithium gallama may be obtained by direct dissolution of lithium in gallium at high temperatures in intermittent and continuous conditions. Therefore, the constructions were developed and two pilot laboratory devices of intermittent and continuous gallama obtaining in metal melts were tested.

The method was developed and pilot laboratory device of intermittent gallama obtaining was made. Its diagram is given in Fig. 1.

The device consisted of the reactor - 1, the reactor cover - 2, the arm punch agitator - 3, the hammer-stone - 4, two connecting branches with cocks (5 – for evacuation of reactor volume, 6 – for puffing inert gas) and the electric motor - 7 connected with agitator rod by a clutch - 8. The gaskets - 9 are inside of the hammer-stone pipe part. In the bottom of the reactor - 1 there is a dimple for agitator rod terminator - 10 serving for centering agitator rotation axis. Details - 1-6 were made of stainless steel of 12X18H10T type, the gasket - 9 is made of teflon. The outside surface of the alloying reactor is covered with current nonconducting mica, supplied with heating elements - 11 and heat insulator - 12. The cover - 2 was set to the reactor body - 1 with six bolts. The perforation degree of agitator blades amounted to 60 %.

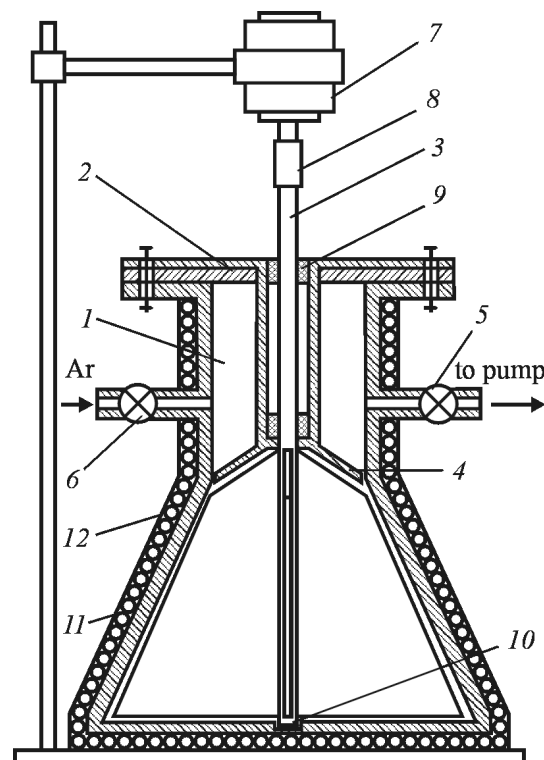


Fig. 1. Draft of pilot laboratory device for intermittent obtaining lithium gallama

The condition of intermittent obtaining lithium gallama was worked out for the given device. Metallic gallium of «ch.p.» classification (with the content of base material of 99,9 %) and metallic lithium of LE -1 type were used in the experiments. The device was placed in a hermetic box inside of which inert atmosphere was generated. Metallic gallium was melted at temperature 50 °C and alloying reactor was filled up with it. The level of liquid gallium did not exceed a half of the distance from reactor bottom to the low end of hammer-stone tapered part. Then metallic (solid) lithium in the amount required for obtaining lithium gallama with concentration of 0,8...1,0 mole/l was placed over hammer-stone tapered part. The gap between reactor walls and hammer-stone tapered part did not exceed $2 \cdot 10^{-3}$ m. The cover of the reactor was closed hermetically. Vacuum pump was

switched on then the cock of connecting branch – 5 connected with it by vacuum tube was opened (in this case the cock for puffing inert gas is closed). Reactor volume was pumped out up to the maximum possible evacuation. After this the cock – 5 of the vacuum pump was blocked and the cock – 6 of argon puffing was opened for generating inert atmosphere in the reactor volume and after this the cock – 6 was also closed. Heating elements supporting heating inside the reactor up to the temperature 250...280 °C were switched on. In a certain time interval (about 5 min) the electric motor turning the agitator at a rate of 2000 rev/min was turned on.

The agitator mixed liquid gallium inside the reactor up to the temperature of 180 °C dispersing it into small drops then liquid lithium as being melted flew down the hammer-stone and contacted with gallium dispersing as well. The form of reactor low part and hammer-stone did not allow rotating melt to rise up the reactor. The agitator rotation supported active stirring of melted metals. The alloying process lasted 10 minutes. After that reactor cover was opened; the obtained lithium gallama was removed from the reactor and analyzed lithium content in it.

A series of experiments in obtaining lithium gallama was carried out in the given conditions. After the experiments the gallama samples were selected; they were decayed with water by the reaction (*) and lithium content in gallama was determined by titration of hydroxide solution. The results of the obtained product analysis showed that in the given device it is possible to obtain in portions lithium gallama of the concentration 0,8...1,0 mole/l required for exchange separation of alkaline elements in the amount sufficient for carrying out research works in laboratory environment. This device possesses, from our point of view, insufficient capacity for supporting gallama requirement at continuous segregation process. Therefore, the attempt to develop the technique and laboratory device for continuous gallama obtaining was made.

The device for continuous obtaining lithium gallama (Fig. 2) consists of cylindrical reactor – 1, the perforated plate – 2, the pressure capacity – 3 with metallic gallium, pressure capacity – 4 with metallic lithium, the capacity – 5 for collecting the obtained lithium gallama and draining capacity – 6 for releasing reactor from agents. Capacities – 3 and 4 have connecting branches – 7. Inside of pressure capacities the cups from fine iron lattice (are not showed in the Figure) are placed for detention of sludge and kish formed in the process of metal melting. The reactor and pressure capacities have flanged joints – 8. The device is provided with conical valves – 9. Between the pressure capacity – 3 and the reactor the transfer pump – 10 supplying gallium at constant rate for supporting gallium column height required for its drop outflow over perforated plate is placed.

Outside the reactor the pressure capacities and communications are isolated with asbestos and mica, provided with heating elements – 11. The device is set at metal frame – 12 supporting steady vertical position of the reactor and pressure capacities. The device is made of chemical-resistant materials.

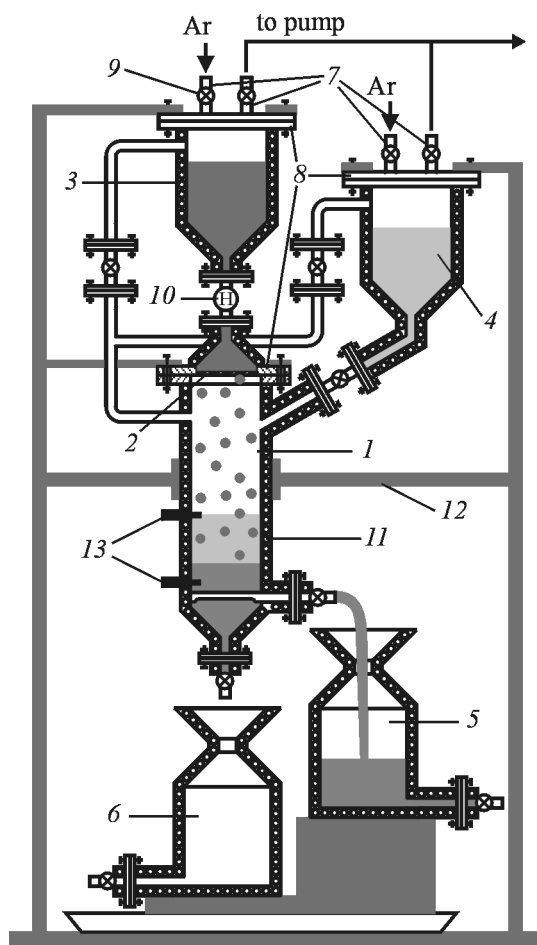


Fig. 2. The draft of the pilot laboratory device for continuous obtaining lithium gallama

Solid gallium and lithium are placed into the proper pressure capacities. The device is blasted with argon from the low part of the reactor to the output connecting branches – 7 of the pressure capacities – 3 and 4 for replacing free air. It is pumped out to the pressure of 10^{-7} Pa and filled up with argon. Heaters supporting temperature of 250...280 °C in all parts of the device are turned on. Gallium and lithium are melted. The reactor is filled up with lithium to the level of 0,18...0,23 m. The pump supplying ~6 l/h of gallium into upper part of the reactor is turned on. Lithium gallama is formed at lithium diffusion into gallium at gallium drop conversion influenced by gravity through lithium layer.

The obtained lithium gallama is accumulated in the lower part of the reactor displacing lithium due to the density difference. In 20 s (time required for reactor filling up with gallama over the level of emptying fitting) the drain valve is opened and gallama is removed from the reactor through the emptying fitting. Lithium gallama serves as a hydraulic lock for liquid lithium closing emptying fitting cave by convex meniscus.

Decreasing lithium level in the reactor it is introduced in portions from the pressure capacity – 4. The thickness of lithium layer is controlled by the level sensors – 13 built in the reactor body.

For organizing uninterrupted lithium and gallium supply into reactor two pressure capacities for each metal connected in parallel are provided in the device. While one capacity is functioning in another one metal is loaded and melted. While emptying the first capacity the device is switched to the second one and in the first capacity metal is prepared to the processing.

The carried out tests of the given device showed that it supports continuous obtaining of 6 l/h of liquid-metal lithium gallama with concentration of 0,8...1,0 mole/l.

Using aggregated similar developed device allows obtaining lithium gallama of specified concentration in the amount required for continuous process of alkali separation in counterflow packed column.

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Conclusions

The stages of phase reversal at alkali segregation by chemical exchange method in the systems LiGa-NaOH and LiGa-KOH have been studied.

Pilot laboratory devices for intermittent and continuous obtaining lithium gallama in metal melts were developed and tested. It was shown that the latter of the stated devices provides obtaining lithium gallama of the specified concentration of 0,8...1,0 mole/l in the amount required for implementation of continuous column process of alkali segregation.

The possibility of organizing phase reversal in gallama-exchange systems LiGa-NaOH and LiGa-KOH and manifold multiplication of single separation effect of alkalis in packed columns was showed.

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Received on 07.12.2006

UDC 666.965:541.182:621

NANODISPERSED SYSTEMS IN TECHNOLOGY OF BUILDING MATERIALS AND UNITS

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The examples of obtaining nanodispersed systems and materials have been given. It is shown that nanodispersed systems are formed at hydration of binders, clay minerals, immediate silica dissolution in soda, different carbonates dissolution in carbonic acid etc. Control of nanodispersed system formation process and using materials obtained artificially in these processes is the main task of structural material science.

Building material technology is connected inseparably with use of disperse systems consisting of solid, liquid and gaseous phases (S + L + G). The main task of the technology is conversion of free-dispersed systems that is the systems with mobile solid phase into connected-dispersed state as a result of serial transformation of the original coagulation structure into condensed one and then into the structure of higher order and strength – crystallization one.

The distinctive feature of building material technology on the basis of dispersed systems is constant presence of solid phase in the system regardless of liquid and gaseous phase presence. Solid phase is a carrier of the main property of building materials – strength; it takes part in

formation of all three types of the above mentioned structures. Solid phase particles are elementary «bricks» which are required for different structures formation; the strength of the latter are predetermined first of all by dispersion and grain-size composition of the particle. The less the particle the less internal defects they contain and such particle presence in the original disperse systems is obligatory. In structure of prepared original dispersed systems (cement paste and solutions, gypsum paste, molding compounds and mixtures, different suspensions etc.) two constituent parts should be distinguished: structural frame formed by coarsely dispersed particles and pore substance consisting of fine dispersed particles and liquid phase placed in pore space of coarsely disper-