Liquid metal based technology of synthesis of nanostructured materials (by the example of oxides). These materials properties and applications areas

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Abstract. Liquid metal technology having some advantages as compared to the other technologies is capable of producing about 100 nano-structured materials. Results of the analysis of properties of synthesized Al₂O₃, In₂O₃, Fe₃O₄, ZnO and other materials show wide scope of their effective application for production of the new types of ceramics, semiconductor sensors, thermal insulation, sorbents and catalysts.

1. Introduction

Nanodimension (or ultra-dispersed) materials are developed at the research centers in many industrialized countries. In the recent three years, total annual funding of basic research programs on synthesis of nanoparticles and nanomaterials and their properties, as well as applied studies aimed at the development of nanotechnologies and related nanodevices in the USA, Japan, Germany, France and other industrialized countries has been about $3 billion. The increase of this amount up to $10 billion is forecasted even by 2010, since definite trend of rapid development of this field of science and technology has been formed recently. There is every reason to anticipate in the nearest future the equalization of the rates of nanosystems and microelectronics development.

World-wide market of high-technology ultra-dispersed materials, as well as instruments and devices made on their basis has not yet been formed, but even now diversified products and wide coverage areas are being formed intensively. According to the estimates made by the international specialists, the higher-priority areas of application of ultra-dispersed nanomaterials and nanotechnologies are as follows: nanoelectronics and nanodevices; synthesis and assembling; biological approaches and applications; dispersions and coatings; materials with large surface area and consolidated materials.

Rapid development of activities in the area of nanomaterial synthesis and creation of nanotechnologies and devices in many countries was mainly caused by the national
nanotechnology programs funded from either governmental or private sources.

Although studies in this area in Russia were initiated as early as in the 1940-ies (by the Ministry of Medium Machine Building), by now there is no State nanotechnology program to join efforts of many scientific and technological centers of the country. Nevertheless, these centers are trying to carry out studies on the synthesis of ultra-dispersed (nano) materials and nanotechnologies, as well as devices and articles within the framework of some low-funded programs (up to 100 million RR per year in total). These programs are run by the Rosatom, the Russian Academy of Sciences and the Ministry of Defense of the Russian Federation. Some of the Russian technologies could be successfully commercialized because of their higher (surpassing) effectiveness or uniqueness.

Work in the area of nanotechnologies and nanomaterials has been carried out since 1992 at the State Scientific Center of the RF – Institute for Physics and Power Engineering named after A. Leypunsky. The basic results have been obtained on the basis of the new technology of nano-material synthesis using experience gained in the area of liquid metal coolants at the Institute for many years. According to the specialists’ estimates, liquid metal technology having some advantages with respect to the other technologies is capable of producing about 100 new types of nanomaterials including oxides, halogenides, nitrides and hydrides of various elements. Some of the above materials have been really produced. These are oxides of aluminum, indium, iron, zinc, molybdenum, magnesium, gallium and tin. Studies on properties of the above nanostructured materials show a wide scope of their effective practical application for production of semiconductor sensors, filters, new types of structural and censor ceramics with improved characteristics, fuel elements for nuclear reactors, super thermal and electric insulation, absorbents and catalysts, etc.

The first statement about the possibility of producing wide range of ultra-dispersed oxides in molten gallium, lead and 44.5% Pb – 55.5% Bi eutectic was made by our specialists at the V All-Russia Conference on Physics and Chemistry of Ultra-dispersed (Nano) Systems (Ekaterinburg, 2000) [1], then, in the papers submitted to Nalchik International Workshop on Thermo-physical Properties of Materials (Liquid Metals and Alloys in 2001 [2], X Russian Conference on Structures and Properties of Metal and Slag Melts [3] and VI All-Russia Conference on Physics and Chemistry of Ultra-dispersed (Nano) Systems (Tomsk, 2002) [4].

At the SSC RF - IPPE studies are successfully carried out on technologies of production of nanomaterials (using methods of plasma-chemical synthesis and selective oxidation of the impurities in the liquid non-alkali metals), as well as articles based on these materials within the framework of not only agreements with Rosatom, but also the projects of International Science and Technology Center (ISTC). By now, the Institute has fulfilled work program on 2 ISTC projects in close cooperation with information exchange with Ohio State University (USA), Los-Alamos National Laboratory (USA), Argonne National Laboratory (USA) and «Forschung Zentrum Karlsruhe» (Germany).

2. Features of liquid metal based technology of nanomaterial synthesis

Traditional method of ultra-dispersed oxide material production is sol-gel method. This method with some features was proposed in 1930 by S. Kistler, Professor of Hanford University, USA as applied to the type of such class materials, i.e. aerogels based on silicon and aluminum oxides. Kistler’s method implies formation of colloid systems in water (alcohol) solutions with further solvent drying-out under supercritical
conditions in the autoclaves. Aerogels of silicon oxide and (less often) oxides of other metals related to nanostructured materials are produced using Kistler’s method in nine research centers in the USA, France, Germany and Sweden for the purpose of research and in two companies, namely: Aeroglass (Sweden) and Thermalux (USA) – on the commercial basis. Industrial application of SiO₂ aerogel mainly implies production of thermal insulation materials for the walls and windows coatings. Effect of light absorption by silicon oxide aerogel in the quarter-wave range has made it possible to prove the feasibility of such nanodimension material as applied to Cherenkov counters.

In contrast to traditional autoclave sol-gel technology, liquid metal based synthesis method developed at the SSC RF – IPPE does not apply damaging or corrosive liquids. Neither is the necessity in maintaining high pressures, thus simplifying systems and components and decreasing significantly their cost. Besides, proposed unique liquid metal technology is notable for its low power consumption rate and high capacity.

Proposed method of synthesis of ultra-dispersed oxides includes two stages:

1st stage. Dissolving in gallium at 323-423 K (or in lead at 653-873 K, or in lead-bismuth at 453-873 K) of metal having higher oxygen affinity than that of Ga (Pb) and solubility in specific liquid metal equal to at least 0.01 wt.%

2nd stage. Oxidation of metal dissolved in gallium (lead or lead-bismuth) by the water vapor according to the following reactions:

\[2\{Ga\} + 3\{H₂O\} = <Ga₂O₃> + 3\{H₂\},\]
\[<Ga₂O₃> \Rightarrow [Ga₂O₃],\]
\[x\{Me\} + y\{Ca₂O₃\} = <MeₓO₂y> + 2y\{Ga\},\]

where \(x\) and \(y\) - stoichiometric coefficients; brackets form characterizes state of reactants and reaction products: \{\} - liquid; [ ] - dissolved; ( ) - gaseous; < > - solid (amorphous).

An overview of well known data on the solubility of metals in gallium, lead and lead-bismuth along with thermodynamic analysis of parameters of reactions of oxide formation in the above solvents show the possibility of production of large amount of MeₓO₂y type composites. For instance, in case of selective oxidation of \{Ga\}-[Me] system at the temperature up to 423 K, the following products are expected: Na₂O, Al₂O₃, MgO and Pr₂O₃. The similar analysis leads to the conclusion on the feasibility of synthesis of TeO₂, NiO, CdO, CoO, Sb₂O₃, As₂O₃, GeO₂, K₂O, ZnO, SnO₂, Na₂O, In₂O₃, Fe₃O₄, Li₂O, SrO, Ba₂O, MgO, Cr₂O₃, Ga₂O₃, CuO, Mn₃O₄, HfO₂, ThO₂, ZrO, Al₂O₃, Pu₂O₃, Y₂O₃, Sm₂O₃, La₂O₃, Nd₂O₃, Ce₂O₃, Ti₂O₅ and U₃O₈ in the liquid lead and lead-bismuth at the temperature up to 873 K.

Diagram in Fig. 1 shows realization of the above method of production of ultra-fine oxides from liquid gallium, lead and 44.5 % Pb – 55.5 % Bi eutectic. Growth of oxide particles into the depth of liquid metal from the surface of bubbling device used for supply of gas-water vapor mixture into the molten gallium (lead or lead-bismuth) is limited and determined by the relationship of forces having different directions (buoyancy, gravity, gas lifting, surface tension, adhesion and inertia).

This unique liquid metal based technology is theoretically capable of producing about 100 various composites. This is proved by the results of thermodynamic analysis of feasibility of formation of the oxide (halogenide, nitride or hydride) phases of metals dissolved in the liquid gallium or lead, or Pb-Bi eutectic and selectively oxidized (halogenide, nitride or hydrogenated) in these liquid metal dissolving media.
The results of the overview of well known data of metal solubility in liquid Ga, Pb and Pb-Bi and thermodynamic analysis are as follows: range of metals having high solubility in liquid gallium, lead and lead-bismuth (≥ 0.01 wt.%) is rather wide; thermodynamic analysis shows that in case of selective oxidation of {Ga}-[Me] system at the temperature up to 423 K, Na₂O, Al₂O₃, MgO and Pr₂O₃ can be produced (listed in the order of probability); similar analytical studies show the possibility of synthesis of TeO₂, NiO, CdO, CoO, Sb₂O₃, As₂O₃, GeO₂, K₂O, ZnO, SnO₂, Na₂O, In₂O₃, Fe₃O₄, Li₂O, SrO, Ba₂O, MgO, Cr₂O₃, Ga₂O₃, CaO, Mn₃O₄, HfO₂, ThO₂, ZrO, Al₂O₃, Pu₂O₃, Y₂O₃, Sm₂O₃, La₂O₃, Nd₂O₃, Ce₂O₃, Ti₃O₅ and U₃O₈ in the liquid lead and lead-bismuth at the temperature up to 873 K; overview of thermodynamic analysis results shows the probability of formation of the following solid chlorides: GeCl₂, CdCl₂, TlCl, MgCl₂, CaCl₂, NaCl and KCl (the sequence is arranged in terms of absolute values of thermodynamic characteristics of material production) as a result of chlorination of {Ga} – [Me] systems at the temperatures up to 423 K; as follows from this very analysis, in case of selective chlorination of {Pb} – [Me] and {Pb-Bi}-[Me] systems at the temperatures up to 873 K production of the following solid chlorides: GeCl₂, CdCl₂, TlCl, MnCl₂, MgCl₂, CaCl₂, NaCl, LiCl, SrCl₂, BaCl₂ and KCl is probable; thermodynamic analysis makes grounds for assuming that treatment of {Ga}-[Me], {Pb}-[Me] and {Pb-Bi}-[Me] systems with nitrogen within the temperature range 473-673 K will result in the synthesis of the following nitrides: Mg₃N₂, Ca₃N₂, Ba₃N₂, AlN, Mn₃N₂, and Fe₃N (this sequence is arranged according to the decrease of probability of material formation); similar analytical studies make it possible to forecast formation of the following hydrides: LiH, CdH, CaH₂, KH and MgH₂ in case of treatment of {Ga}-[Me], {Pb}-[Me] and {Pb-Bi}-[Me] melts with hydrogen containing mixtures at the temperature 473-673 K.

By now, the following ultra-dispersed oxides: Al₂O₃, Al₂O₃·H₂O (aerogel), In₂O₃, Fe₃O₄, MgO, MoO₃, SnO₂, ZnO and Ga₂O₃ have been produced by the method of selective oxidation of metal impurities in liquid gallium, lead, and lead-bismuth. The form of synthesized materials is powder with macro particles up to 500 μm size and aerogels having linear dimensions of samples up to 10 cm. Dimensions of structural components of ultra-fine oxides are within 5 nm to 200 nm range depending on chemical composition of produced materials and their synthesis conditions.

Because of their nanostructured state synthesized materials are unique from the standpoint of creation of thermal and electrical insulation, sensors, ceramics, nuclear fuel and catalysts with improved technical and economical characteristics.
3. Results

In the course of studies we have shown that oxides of indium, gallium, tin and zinc synthesized by liquid metal technology (micro structure of ultra-fine ZnO is shown in Fig. 2) are semiconductors with a peak sensitivity to gas from the standpoint of improved micro system sensors of ozone, hydrogen, chlorine and other gases in the air. Sensitivity of these sensors to ozone is $1 \times 10^{-7}$ vol.%, i.e. an order of magnitude higher than that of the best foreign and domestic commercial specimens. It has been demonstrated in some other studies that MgO, MoO$_3$ and Fe$_3$O$_4$ oxides in nano-structured form are more effective catalysts of some reactions of the oil-chemical synthesis as compared to the usual oxides of the same chemical composition.

In the course of studies carried out for a long time period the authors of the article have developed method of synthesis of aluminum oxide (composition Al$_2$O$_3$·H$_2$O) from liquid gallium. This material is produced as aerogel, i.e. it has volumetric macro structure. Evaluated specific weight of flaked aerogel bodies made taking into account weight and approximate volume of specimens is $0.013 \pm 0.080$ g/cm$^3$. Taking into account density of crystalline aluminum oxide of $\delta$-modification (~ 2.4 g/cm$^3$) porosity of material was evaluated as $96.7 \pm 99.5$ vol.%. The micro structure of initial specimens of amorphous aerogel and those subject to thermal treatment is formed of like-directed threads. Their dimension (conventional diameter) ranges from 5 nm to 100 nm. Thermal conductivity of aerogel is record low (0.01-0.02 W/(m·K)) within the wide temperature range (130-1500 K) thus determining attractiveness of its use as super thermal insulator.

There are also other important features of aerogel made on the basis of aluminum oxide. It has been revealed that specific electric resistance of the aerogel is rather high (>10$^{10}$ Ohm·m), this determining prospects of the development on its basis of the new class electrical insulation materials. It has been revealed also that aluminum oxide aerogel is a promising absorbent capable of replacing activated carbon and even aluminum oxide for separation or absorption of saturated hydrocarbons and industrial gases (CO, CO$_2$, NO and NO$_2$), as well as expensive absorbents used for purification of the liquid radwaste. Small admixtures of aerogel (within 1 wt.%) into matrix powders at the stage of production of ceramics: SiC, Si$_3$N$_4$, ZrO$_2$, UO$_2$ etc. make it possible to produce structural and sensor articles and nuclear fuel (fuel elements for NPP) with higher strength (by 20-200%).
Based on the above information, the following advanced areas of application of ultra-dispersed oxides synthesized from liquid Pb, Pb-Bi and Ga can be identified: development of special thermal and electrical insulation; development of high-temperature ceramic materials having high strength (for the use as structural materials, nuclear fuel elements, sensors for detection of impurities in the liquid metals etc.); development of new absorbents for purification of liquids and gases; creation of sensors for gas control (ozone, hydrogen etc.); development of the new generation of catalysts and their carriers for application in chemical production plants.

Authors of this article now carry out studies on production of ultra-dispersed halogenides, nitrides and hydrides in the liquid gallium, lead and lead-bismuth, as well as expansion of the range of synthesized nanostructured oxides.

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