Preparation of Research and Manufacturing in A Micro-g Environment

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Abstract- **In this article was examined the aspects that would have an effect on development and research of the technology of crystal production in space in the near future. New raw material for space additive manufacturing is proposed. The important aspects of the 3D-printing in Deep Space Missions are determined. The most effective methods for study and produce the crystals are defined as well. In a micro-g environment there is an opportunity to provide container-less retention of the melt. A classification of the methods for melt stabilization in three dimensions during crystal growing process is made, and the prospects and limitations for each of them are mentioned. In addition, the criteria for selection of perspective objects are determined for the future space research and production, such as crystals of sillenites and diamonds.**

Keywords- Space 3D-printing; Diamond; Sillenite

I. INTRODUCTION

For space research the intermediate phases with temporary return of the objects being under study to Earth result in a considerable increase in value of final result and time spent. Therefore, for really perspective in-situ research of the substances in space (for instance, to determine optimum parameters of future space crystals productions) it is reasonable to provide an orbital laboratory with maximally complete set of equipment. Cost of instruments delivery increases in direct proportion to their mass. The limiting factor is an available volume under launch vehicle payload fairing as well. There is a necessity to combine them into complexes with common uninterruptible power systems and common cooling systems (including, pipelines for circulation of cryo-coolers). The most rational approach is to use new on-orbit opportunities. Extremely low values of residual pressure outside the spaceship remove a part of factors, which limit the dimensions of vacuum chambers of the research instruments. Most bulky vacuum pumps and very thick walls are unnecessary for outside vacuum chambers. The increased dimensions may allow keeping in vacuum a large quantity of samples prepared for measurements. It is a good basis to ensure continuity of the measurements without expenditures of time for replacement of the samples with concomitant operations (i.e. vacuuming, heating or cooling of instruments' operational elements, etc). A micro-g environment also gives specific opportunities to minimize contact of test substance with the instruments at its fixation in measurement bay. This is of the utmost importance for mid-IR region spectroscopy, in which selection of the material for windows always was compromise in terms of transmittance performance, ease of use and price. The factors that limit the possibilities of utilizing the windows are as follows: low moisture resistance (NaCl, KBr, CsI), limited spectral range (MgO, α-Al_2O_2, ZrO_2), high toxicity (Thallium salt KRS - 5), non-transparency at high temperatures due to free thermal electrons (Si, Ge), extremely high cost (Diamond). Usage of composites, such as Germanium-coated KBr, resolves only a small part of problems.

After the age of global research and definition of the main classifying signals of the substances a further detail of knowledge is needed. Today, a precision study of the properties of insignificantly modified materials with fixation of relatively weak effects has become a basis of most commercial projects. Directions of the activities are often picked to make insignificant patent improvements and sell the product under new brand name based upon well-known object that has long proved characteristics. At the present time, there is a need for techniques of measurement of high-clean substances or the ones with exact ratio of the components without casual composition changes during preparation of the sample. Typical requirements are a highly inert storage volume, absence of thermal- and photo-initiated reactions with the volume components and contaminations on the surfaces, which would change the test substance; total removal of previous sample remains on reusable elements or economic validity of utilizing the expendable ones; a lack of excessive distortions of sample's weak signals under background signals. If there is no window material that meets all the requirements it is possible to refuse the windows and cell for fluid analysis. Generally, in a micro-g environment the shape of liquid drop is specified by surface tension forces. In orbital flights it has been already proved that it is possible to stabilize large spheres of liquid in three dimensions by means of metal loop. Having a small quantity, liquid distributes in the loop in the form of virtually flat film. Surface in the middle of the loop remains virtually flat even when quantity of liquid varies. It is a good basis for production of samples' infrared spectrums without background noises. Depending on liquid volume, a diameter of radiation beam is adjusted on condition that it is less than diameter of the loop. The material of loops intended for keeping the liquid samples should be maximally inert and easily cleanable; the best material for that purpose is platinum.

II. SPACE ADDITIVE MANUFACTURING

International space agencies are seriously considering the possibility of rapid prototyping technologies in microgravity. 3D-printing builds a solid object from a series of layers, each one printed on top of the last – also known as additive manufacturing. The evolving additive manufacturing for use in space and on Deep Space Missions Projects include 3D-printers testing in orbit. National Aeronautics and Space Administration (NASA) plans to use melt deposition modelling additive manufacturing in the microgravity environment of the International Space Station (ISS) [1]. European Space Agency (ESA) has an analogous project called Additive Manufacturing Aiming Towards Zero Waste & Efficient Production of High-Tech Metal Products (AMAZE project) [2]. Absence of vibrations typical for rocket launch can simplify the construction 3D-printed structures, in some cases not even strong enough to support their own weight on earth, yet fully functional in microgravity. There are some parts of the spacecraft, which is very difficult to be compacted under rocket fairing. Not always possible to decompose these structural elements in space. For instance on spaceship Galileo a collapsible mirror was not opened, and communication with the ship was provided with the help of low-power reserve antenna. As a result, the ship control and data reception were considerably complicated due to a great distance from Earth [3]. There is enough time on Deep Space Missions to create irregular shaped parts (frame structure and parabolic antenna mirror) by additive manufacturing methods. Selection of raw materials for rapid prototyping technologies is very important, and sets limits for future technological possibilities. The main titanium alloy Ti-6Al-4V has advantages due to its wide use in the space industry. However, instead of titanium powder as a raw material is better to use a brittle titanium hydride. It is possible by using the hydrogen (from the fuel system, for example) to hydrogenate the broken titanium product for successful grinding. Towards zero waste production, a damaged titanium part would go into a raw material for the end 3D-printed replacement, rather than having to wait for the arrival of the next supply ship. The large surface area of titanium hydride accelerates chemical reactions Fig. 1.

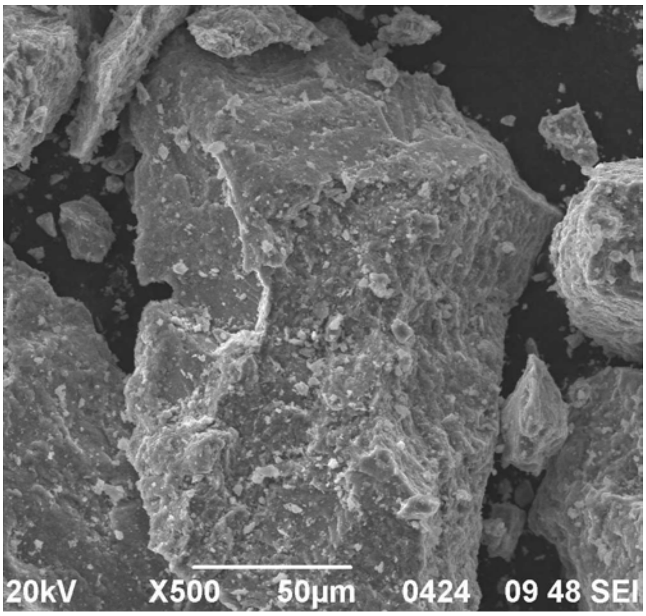

Fig. 1. The surface of powder titanium hydride (secondary electron image).

This is good for the synthesis reaction of titanium nitride from TiH_2 powder combustion in a nitrogen atmosphere. However, this creates problems during the oxidation in the air. Therefore, the most successfully applied technology is dehydrogenation and sintering compacts in vacuum. Powder sintered composite Ti-6Al-4V/LaB_6 created for the nuclear industry using this technology has reached the level of cast Ti-6Al-4V alloy [4]. In general, the addition of 0.08 weight % boron in the weld seams and 3D-printed details may be effective hardening method, without loss of ductility of titanium alloys. Porosity problem solved by filling the pores by LaB_xO_y & TiB chemical compounds Fig. 2.

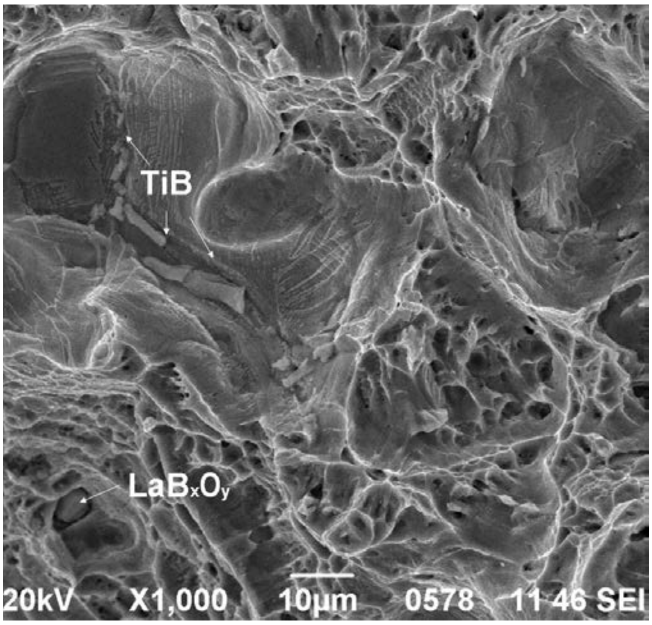

Fig. 2. Picture of surface destruction in Ti-6Al-4V/LaB_6 composition (secondary electron image).

They can also hinder the growth of the grains of the alloy that is important for the cast alloys and powder metallurgy, as well as for welds and products created by additive manufacturing methods [5]. Space 3D-printing in vacuum overboard the spaceship allows to create a metal product without an oxide film on the surface. This simplifies the acoustic emission signal processing, by reducing the amount of information coming from the sensors. Absence overlay of signals from the oxide film cracking and the base metal destruction, enhances the capabilities of non-destructive testing of metal parts [6, 7]. Such opportunities for quality assurance are very important for titanium alloys and principled for aluminium alloys.

III. CRYSTAL GROWING PROCESS

At the present time, Travelling Liquidus-Zone method (TLZ) [8], Detached Bridgman [9], and the Floating Zone melting [10] are generally used for production of the crystals on orbit. TLZ is also suitable for precision cleaning at multiple passing of molten zone along the sample and just for a single crystal growing at single re-melting. However, in this method during the contact of growing crystal with crucible walls the number of impurities and structural defects is considerably increased. The microgravity allows implementing the methods for melt retention to grow the crystals without the contact with crucible walls [11]. But anyway, there is a necessity of minimum contact with the melt for its stabilization in three dimensions.

IV. MICRO-G ENVIRONMENT MELT STABILIZATION METHODS

Most techniques for the containerless retention of small drops of liquid (~ 3 mm) on earth after modernization are acceptable for stabilization of large volumes of liquid in space. At the same time, the less impact on the melt, the less its residual vibrations affect the quality of growing crystal. The methods for stabilization of the melt in the center of working chamber under microgravity conditions can be divided into aerodynamic, mechanical and electromagnetic ones.

A. Aerodynamic Retention of The Melt:

- Systems of control exhaust hoods and nozzles by high-clean gas flows.

- Stabilization by sound waves in high-clean gas.

The aerodynamic methods require on-line control of the parameters of inert atmosphere full of melt fumes. Sensors for qualitative and quantitative control of evaporating elements can be installed in control air vents Fig. 3. With the help of saturation of inert gas flow from control nozzles by alloying elements it is possible to limit the evaporation rate for necessary melt elements. The flows from nozzles, air vents and the melt surface can be visualized by Schlieren photography (or video) methods. At the same time, it is possible to receive objective data on aerodynamics of gases around the melt drop, as well as on interaction of shock waves and the melt during sound stabilization. The sound stabilization is acceptable only for those liquids, in which the sound of given frequency does not cause cavitation. On Earth the bubbles are removed from liquid under buoyancy force, but in space it does not happen. Therefore, the bubbles of gas can be caught by growing faces of the crystal.

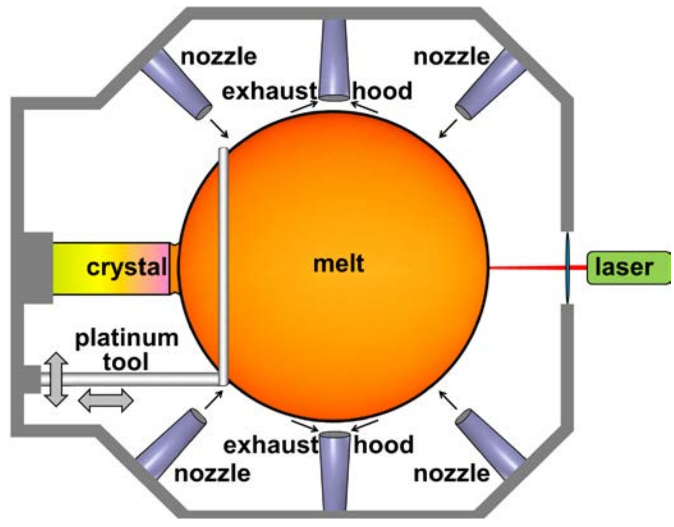

Fig. 3. Schematically represented conception of the crystal growing, with combined aerodynamic (exhaust hoods and nozzles by high-clean gas flows) & mechanical stabilization (platinum tool with the loop) of melt heated by laser through the sapphire window.

B. Mechanical Stabilization Prospects:

- Heater plunged into the melt, which is located near the seed crystal, makes possible a precision and control of temperature conditions of the crystallization in a local area of solution. If the heater is located far from the seed crystal, it is possible to stabilize location of the melt drop at the expense of adjusted movements in three dimensions.

- Stabilization is possible, using a platinum tool with the loop (Fig. 3.), at the cost of surface tension forces as in preliminary experiments to study liquids in microgravity.

- Stabilization by adjustment of the seed crystal provides almost contactless interaction with the melt Fig. 4. Therefore, it considerably reduces, but does not except, the impurities and crystal nucleation. However, movements of the seed crystal can result in disturbance of local area of a liquid alongside the growth region.

C. Electromagnetic Methods Are Applied for Retention and Flash Smelting of Rare or Easily Oxidable Metals (V, Nb, Ta, Ru) with The Help of Field Magnet (induction heated melt Fig. 4.).

For the melts with characteristics inappropriate for stabilization by the magnetic field it is better to use the heating equipment that will not create additional eddies at aerodynamic stabilization methods. A laser heating of the melt through the sapphire windows in working chamber can provide a maximum distance between heat source and the melt.

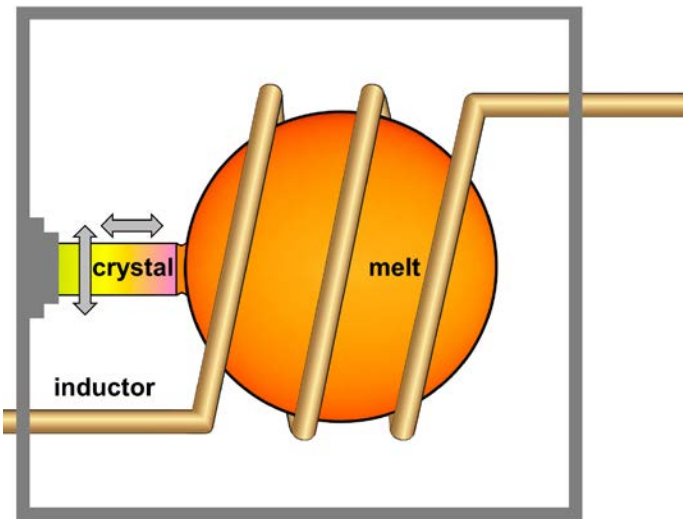

Fig. 4. Schematically represented conception of the crystal growing, with combined electromagnetic & mechanical stabilization (adjustment of the seed crystal) of induction heated melt.

A lack of contact between the melt and equipment decreases a diffusion heat transfer due to the absence of heat abstraction through the crucible walls. However, under microgravity conditions the almost total lack of convection and sedimentation (settling) plays a major role in minimization of concentration heterogeneities during the delivery of molecules to the surface of growing crystal [12]. To eliminate effect of heat-gravitational convection on earth during crystal growing from large volume of the melt is practically impossible [13]. At a single crystal growing from the melt under heat-gravitational convection there is an intense movement of the melt, which is eddy and leads to fluctuations of temperature and rate of mass fluxes near the interphase boundary. At the same time, it leads to fluctuations of solidification rate and occurrence of micro-inhomogeneity in the distribution of impurities and structural defects in the volume of growing crystals. In a micro-g environment the thermo-capillary convection mechanism only remains at the expense of changing the surface tension due to uneven heating (Marangoni convection).

At a low growth rate the most favorable conditions for homogeneous radial distribution of the impurities are a lack of convection and vibrations [14, 15]. There are so many advantages for those trends of space production, in which it is necessary to grow large-sized crystals or where the critical parameter is a uniform distribution of alloying elements [16]. On earth it is technologically easier to grow small crystals with a high growth rate. In view of the aforesaid, the following two prospective trends of space research and production are above all others:

- Growth of sillenite crystals from liquid phase
- Growth of coloured diamonds from gas phase.

V. SILLENITE GROWING PROCESS

The sillenites with general formula $Bi_{12}MO_{20}$ (where M=Si, Ge, Ti and Zn, B, Ga, Fe, Tl, Cr, Mn, P, V in combinations which give valence of IV) have a unique combination of optical (Pockels effect, visible photoconductivity, Faraday effect, as well as piezoelectric, acousto-optic, photo-reactive and magneto-resistive effects) and electro-physical properties (electret effect and dielectric anomalies). In addition, the properties can be modified due to alloying. For instance, the Sn allowing of sillenites by diffusion method will cause an increase of photosensitivity of the crystals. Due to a high concentration of defects in sillenite crystals the alloy additives are required to be added in large quantities for considerable change of sillenite properties. At the same time, a considerable increase in concentration of alloy additive complicates the process to obtain homogeneous crystals. In some cases the annealing is carried out either in oxygen or in vacuum to impart specific properties to the crystals. However, the annealing of stoichiometric crystals $Bi_{12}SiO_{20}$ and $Bi_{12}GeO_{20}$ under such conditions leads to bismuth de-enrichment. At the same time, crystal photosensitivity and visible absorption coefficient are decreased. The photosensitivity of germanium and silicon sillenites, which are grown from the melt by Czochralski method in the form of large-size ingots, is decreasing from the seed area to the separation area. It should be noted that the reduction of density to the end of ingot is typical for crystals $Bi_{12}MO_{20}$. In cross section a density in the center of crystal is higher. Taking into consideration that the pressure of Bi_2O_3 vapor at $Bi_{12}MO_{20}$ melting temperature often is higher than the pressure of other oxides vapor, it was concluded that the melts, from which the single crystals are grown, are de-enriched by bismuth oxide. To resolve these problems typical for the Earth, which is caused by considerable difference in atomic mass of mixture components; the experiments on sillenite growth on orbit are being conducted. The researchers have already grown on orbit the stoichiometric crystals $Bi_{12}GeO_{20}$ on board the space shuttle (flight STS-77, flown in May 1996) [17, 18], as well as crystal $Bi_{12}SiO_{20}$ doped by Ce [19, 20] that has higher quality than check samples on the Earth. However, the huge reserves still remain to update the techniques for growth of large crystals, especially at container-less retention of the melts in a micro-g environment.

VI. DIAMOND GROWING PROCESS

The growth of small diamonds ~ 1 carat is a successfully solved task on the Earth. At the same time, growth of large crystals with a very uniform distribution of colouring impurities (for example, boron for blue colouring) can be prospective in space. The main advantage of spaceships is their long isolation from the impact of extraneous factors and minimization of vibration action. However, it does not concern manned orbital space stations [21].

The pioneers in the research based upon decomposing carbon-containing gases on the diamond seed at pressures $\leqslant$1 atmosphere were Eversole and Deryagin. After their works many trends in gaseous-phase synthesis have been found. The methane is very often used as a source of carbon [22]. However, there is an opportunity to use CO as a carbonaceous substance for diamond synthesis. Activity of CO molecules sharply rises when they are a part of carbonyl complexes. That is confirmed by a significant reduction in oscillation frequencies ν_{CO} in the infrared spectra of these compounds [23-26]. During thermolysis of vapour $Re_2(CO)_{10}$ at t=920 degrees Celsius and pressure equal to 0.01 mm Hg there was a growth of diamond seed crystals up to 0.5 – 1 mg in ten hours [27]. Thus, it was shown a possibility of disproportionation of CO molecules with the formation of diamonds. During the study of the properties of various heteronuclear clusters of platinum metals it was revealed that at a spontaneous decomposing some of them the diamonds are formed [28]. In particular, heteronuclear platinum-palladium carbonyl clusters $Pt_xPd_y(CO)_Z$ have such an ability. The boron as alloying element can be added in the phase of synthesis of platinum metals' carbonyl clusters. Another method, which allows using the elemental carbon in place of its compounds, is based on giving the acceleration to carbon ions up to high energies in an electric field [29, 30].

However, the attempt to provide a high rate of diamond film growth has failed. The time of growing process is limited by the necessity of periodic removal of graphite on the surface of growing diamond. This is done by the annealing either in oxygen or in hydrogen atmosphere under pressure. The burning of graphite by high-energy particle fluxes or lasers is also possible. A suppression of graphite layer nucleation by high-intensity light of gas-discharge lamp saves the total time of crystal growth process. In the attempt to speed up the process of crystal growing an epitaxial growth of the mixture of fractal structures with different types of hybridization of the valence electrons (sp^3,

sp^2, sp) takes place instead of diamond film formation [31]. The long growth of large-sized single crystals of the diamond from gas phase can occur on board the satellites during their typical average service life ~ 5 years. After the end of service life of the satellites with equipment intended for crystal growth the diamonds can be delivered to earth, using small X-39B-type [32] shuttles. Low growth rates are preferable for obtaining the artificial diamonds, almost equal to real, without visible boundary between the seed crystal and overgrown layers. This technique is also prospective for the growth of color diamond coatings for gem-quality cut diamonds of large size. However, this process takes much time because the highest rates of epitaxial film growth are attainable only for small crystals. Moreover, the thickness of coloured layer must have a margin in reliance on additional cutting of coloured diamond. For further development of the above-mentioned techniques there is also a need for further analysis of gas dynamics by Schlieren photography methods during the growth of epitaxial films both on earth and in microgravity in the absence of convective streams.

VII. CONCLUSIONS

For appropriate assessment of the prospects for space research and manufacturing it is necessary to keep in minds the following aspects:

1) Ti-6Al-4V/LaB_6 composition may be a promising for space additive manufacturing;

2) The methods for stabilization of the melt in microgravity for crystal growing are divided into aerodynamic, mechanical and electromagnetic ones;

3) The growth of sillenites in micro-g environment is an effective way to provide a uniform distribution of the components;

4) At low growth rates it is possible to obtain high-quality diamonds on board the satellites.

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