German-Moldovan Workshop on Novel Nanomaterials for Electronic, Photonic and Biomedical Applications, Chişinău, 7-8th of July, 2011

Perspectives of Single Cast Nanowires Technology

Anatolii IOISHER[1], Efim BADINTER[1], Nicolae LEPORDA[2] ,
Vitalie POSTOLACHE[1], Eduard MONAICO[3], Ion TIGHINYANU[2]
[1] *Institite "ELIRI"(Chisinau), ioisher@eliri.md, bad@eliri.md,*
[2] *Institute of Electronic Engineering and Nanotechnologies, Academy of Sciences of Moldova*
nicul@lises.asm.md, tiginyanu@asm.md
[3] *National Center for Materials Study and Testing, Technical University of Moldova,*
m_eduard_y@yahoo.com

***Abstract* – The paper is dedicated to production potential of glass-coated cast nanowire with metal-, semimetal- and semiconductor-based cores by means of Taylor-Ulitovsky method. Criteria of melted core-formative material penetration into a drawing capillary were analyzed. Theoretical preconditions of the reduction of cast microwire diameter up to nano-dimensions of core are reviewed and an improved method of cast nanowire manufacturing is proposed. Correctness of conclusions was experimentally proved and laboratory samples of micro- and nano-wires with core diameter of about 200-300 nanometers were produced, even in case of materials with poor adhesion.**

***Index Terms* – nanowire, cast microwire, glass insulation, electromagnetic field.**

I. INTRODUCTION

Rapid development of nanotechnology, including various aspects of application, has led to an increased interest in production of glass-coated micro- and nanowires with core diameter less than 300 nanometers [1]. Such micro- and nanowires can find application in the field of medicine and biology, e.g. for the development of miniature sensors and probes, including thermoelectric ones, ecological small power engineering and electronics for binding nano- and micro-objects and other branches of science and engineering.

The process of cast micro- and nanowire production is known to include the following:

- melting of a definite amount of conductive material (metal, semimetal, semiconductor) placed into a glass tube in a suspended state at electromagnetic (EM) field of a high-frequency inductor;
- heating and softening of the glass pipe end owing to thermal contact with a molten drop of conductive material and forming a microbath in the form of softened glass which is flowing round this levitating drop;
- pulling down of the lower end of that coating (for instance by means of coiling onto a spool) into a capillary, which is later on filled in with the said conductive material from the microbath that is a core-formative material;
- cooling of the pulled down filament, which after crystallization of core and glass forms the said glass-coated cast micro- or nanowire.

Attempts of production of super-thin glass-coated cast microwires (by means of Taylor-Ulitovsky method [2]) with core diameter less than 1 micron have been undertaken since early 70 of the past century, when nano-technology was not so advanced [3]. Such microwires, especially semimetal- and semiconductor-based ones, were of interest from the view of solid-state physics, as a sample of quasi-one-dimensional crystalline object. Quantum dimensional effects have been investigated on the basis of microwires with small core diameter and a number of interesting results have been obtained [4, 5]. However, such microwires have not found practical application. Some components and devices made on the basis of super-thin metal- and metal alloy-based microwires confined themselves to laboratory samples such as, for instance, radiation electrometer involving conductive and mechanical properties of such microwires.

Due to the abrupt reduction of production and application of cast microwires in nineties, investigations on manufacturing methods of such microwires have been stopped. Though nowadays there is a revival of interest in some types of such microwires, especially magnetic ones [6], casting technology still remain insufficiently investigated. Potential of further reduction of microwire diameter and estimation of prospects of cast nanowire production are reviewed in the present report.

II. RESULTS AND DISCUSIONS

Theoretical and experimental studies of glass-coated cast microwire production have demonstrated that core diameter as well as overall diameter significantly depend on such physical parameters of applied materials, as dynamic viscosity η and surface tension σ_g of glass within the temperature range investigated, interfacial tension on glass-coreformative material border σ_{mg} within the area of microwire formation, density of materials used for microwire casting, as well as on rate of microwire drawing v_s and some other technological parameters. Many of the abovementioned parameters depend on temperature T of casting process and in a complicated way on main technological parameters [2].

The mass of the drop of core-formative material M forming (along with covering softened glass-coating) the so-called micro-bath is of great importance too. This drop is at a suspended state because of ponderomotive forces of high-frequency electromagnetic field (EF) of inductor and pressure difference Δp under and over the micro-bath (owing to glass-tube rarefaction). The weight of the drop M_k, suspended only by EF, is called critical one. If $M > M_k$, the microwire core diameter is to a greater extent defined by thermophysical parameters of glass and rate of microwire drawing [3, 7]. At that glass tube feeding rate v_g, geometry and rarefaction, density of core-formative material γm and configuration of intensity of electromagnetic field over and below inductor is of a great importance for microwire geometry formation.

Over the time of broad application and research of cast microwires with resistive core, diminution of the core diameter as much as possible has been considered mainly in order to increase microwire linear resistance. In the framework of Zotov's theoretical model [7], the dependence of microwire radius r (which is considered as a homogenous filament) on a number of physical parameters of glass and microwire drawing rate (in case of not so great rates) has been deduced:

$$r = D/2 = 0{,}9\eta^{2/3} / (\sigma_g^{2/3} \cdot v_{dr}^{1/3} \gamma_g), \quad (1)$$

where γ_g – glass density. Here D should be considered as an overall microwire diameter, though the authors regard it as the core diameter.

If the weight of drop of melted core-formative material in the micro-bath is less than the critical value, then the authors of the present work define semiempirical dependence of core diameter d on a number of technological parameters, which have a direct impact on the geometry of forming micro- and nanowires and which may be regarded as governing parameters of casting process [8]:

$$d = k_T \eta_g^{4/3} / (\gamma_g \sigma_g^{1/3} v_{dr}^{2/3}), \quad (2)$$

where v_{dr} is capillary drawing rate; k_T – nondimensional empirical coefficient dependent on a number of additional technological parameters (in case of our experiments $k_T \sim 1\cdot10^{-6}$, all the values of physical parameters are expressed in SI units). The empirical formula (2) is close to theoretical formula (1) in terms of structure, though its distinguishing feature is stronger power dependence of diameter on glass viscosity.

As evident from both mentioned formulas, the lesser glass viscosity and greater casting rate the lesser microwire diameter becomes without limitations. Having ensured a great rate of microwire coiling onto a spool and decreasing glass viscosity, for instance by means of increase of operating temperature of the micro-bath, cast nanowires with core diameter less than 100 nanometers might be produced. As long ago as in eighties of the past century the authors of the present report have managed to produce microwires with ultra-thin bismuth-based core with core diameter within the range from 80 up to 300 nanometers by means of the said method. But at that time the overall diameter of the produced microwire was over 30 - 40 microns. Its casting method was unstable, the core diameter fluctuating within a broad range (up to 300 %), and such a super-thin microwire was able to be made of two core-formative materials with perfect adhesion to glass only. Having selected samples with required diameter, such microwires (with core made of Bi and Bi-based alloys with **Sb, Pb** and **Sn**) were used for research of their physical properties (as quasi-one-dimensional objects) [4, 5].

It must be however emphasized that the mentioned formulas (1) and (2) are correct only for a definite range of casting rate and some other technological parameters, such as glass tube feeding rate, its overall dimensions, microbath temperature range and others. Thus, in the case of increase of rate v_{dr} , starting from 1,5 m/s, at other fixed parameters, some increase of core diameter with further stabilization at higher rates has been observed instead of decrease of the said parameter. (Especially when weight of drop is over the critical value). This is indicative of the need in further investigation of Taylor-Ulitovsky process in order to define potential and requirements of production of long single cast microwires on the basis of various materials.

Currently there is no comprehensive theory unambiguously describing interconnection and interdependency of different technological and physical parameters affecting the process of microwire casting and final properties of microwire (and, perhaps, there will be no ever owing to its extremely complexity of the process). Accordingly, there is an unsolved problem regarding ultimate potential of this manufacturing method and minimal achievable core diameter. Thus, it would be expedient to divide description of microwire casting process by means of Ulitovsky method into separate partial problems which can be solved easier regarding tasks put by later on.

In order realize this let us formulate two main sub-tasks:

1) determination of the criteria of initial penetration of melted core-formative material into forming capillary and extreme allowable diameters of such a capillary;

2) revealing of input values physicotechnological parameters of casting process ensuring combined drawing of glass capillary with minimal diameter and melted core-formative material filling in this capillary with further crystallization.

When melted core-formative material (let call it metal) penetrates into capillary the main role is played by the following: 1) capillary effect due to the surface tension of metal; 2) inter-phase tension on a border glass-metal; 3) pressure over a melted metal inside of a glass-tube of a micro-bath; 4) dimensions of drop of melted metal (to be more exact, height of drop of melted metal in a micro-bath H_m over the point of penetration point into a capillary), forces which carry metal, induced by downward movement of walls of primary stretching cone and metal adhesion to glass. It is worth to be pointed out that in the upper part of the primary stretching cone the speed of wall movement is slow enough and it does not exceed $(2\ldots5) \cdot v_g$, where v_g – the rate of glass tube feeding into inductor area. Correspondingly, carrying force F is also weak; it rises in its bottom part and in the beginning of the secondary stretching cone.

It is especially worth to emphasize that the internal diameter of forming capillary $d = 2r$ is mostly defined by variable radius $r_c(x)$ of primary stretching cone, giving onion-like shape to drop of metal and microbath in a whole (x – is vertical axe). In the report of Yu. Chugaevsky [9] it was obtained the theoretical relation describing the shape of the mentioned primary cone:

$$r_c^2 = R_0^2 + \left[x - \frac{2H}{1+2\ln(r_c/\xi)}\ln(R_0/r_c)\right]^2, \quad (3)$$

where R_0, H – radius and height of molten drop, ξ - radius of a conditional column of melt on which ponderomotive force of electromagnetic field does not operate,.

Derivation of the obtained formula assumes by default that the weight of the drop is completely counterbalanced by ponderomotive forces of electromagnetic field of inductor excluding a thin cylindrical “rod” with radius ξ along axis of the drop. The weight of this rod $P = \pi\gamma_m gH\xi^2$ generates vertical pressure along axis of area of capillary formation and it is along with pressure difference over the drop of melted metal both inside of capillary and under it $(p_0 - \Delta p)$ one of the component forces, promoting penetration of metal into the capillary. Here γ_m – density of core-formative material, g – acceleration of gravity, p_a – atmosphere pressure, Δp – rarefaction inside a glass tube over a microbath.

The said model does not take into account horizontal component of metal pressure on glass coating of a primary stretching cone, which significantly impacts on the diameter of the said cone and, in the end, on the diameter d of stretching capillary in comparison with expected one in accordance with calculation.

As is well known, the high-frequency field of inductor (both cup-like and multi-coil one) has a singularity along the vertical axis where expulsive force equals to zero. Correspondingly, in case of suspended melt of metal within the bottom part of incipient drop a special area is formed (a “black spot” in a way), where ponderomotive forces do not impact on that drop and the weight of this part of the drop can be counterbalanced by cohesion and surface tension of metal σ_m only, while during microwire casting it can be counterbalanced by surface tension of glass σ_g, as well. A definite impact on balance of forces influencing on metal inside of the microbath is contributed by the abovementioned pressure difference $(p_0 - \Delta p)$, if pressure inside of an empty capillary is close to vacuum gage pressure.

Experiments carried out during microwire casting show that in the case of metals with low capillary constant $a = 2\sigma_m / (g\,\gamma_m)$ (e.g., **Pb** and **Bi**), the metal drop is likely to leak out of a microbath. This takes place, e.g. during Bi-based microwire casting at every slightest vertical oscillation or insufficient glass viscosity close to the bottom of a microbath. We suppose that it takes place when the diameter of a primary stretching cone in the bottom part is greater than some critical value, which exceeds 2ξ, i.e. dimensions of a “black spot” of expulsive forces of electromagnetic field of inductor. Usually, it lays within the range from 0.05 up to 0.2 mm.

As a first approximation balance of forces at entrance to a stretching cone impacting on penetration of metal into a capillary can be presented in the following way:

$$F_1+F_2+F_3= F_4, \quad (4)$$

where forces promoting penetration of metal into a capillary are listed on the left, while forces preventing from that are listed on the right. Here:

$F_1 = (p_0 - \Delta p)\cdot\pi r^2$ – force, caused by pressure difference over and below drop of melted metal in a microbath;

$F_2 = \pi\,\gamma_m\,g\,H\,r^2$ – force of pressure of column of melted metal with height H on its surface at entrance to a capillary (this height depends on diameter and shape of drop of melted metal in a microbath);

F_3 – carrying force related to movement of walls of the primary stretching cone and adhesion of metal to glass. Taking into account that this force must ensure acceleration of column of melted metal from close to zero speed up to speed v_s of capillary pulling drawing, it is easy to show that

$$F_3=(\pi/2)\gamma_m v_s^2 r^2;$$

$F_4 = 2\sigma_m r$ – forces of surface tension of metal on a border metal-vacuum inside of glass capillary.

With the help of the abovementioned formulas it can be shown that the radius of capillary a core-formative material can penetrate in is defined by the following equation:

$$r = 4\sigma_m / \{\pi\,[(p_0 - \Delta p) + \gamma_m\,g\,H + \gamma_m v_s^2]\}. \qquad (5)$$

As it can be seen from (5) in case of reduction of surface tension of metal σ_m and increase of capillary drawing rate v_s reduction of diameter of microwire to be obtained $d = 2r$ can be achieved without any limitations, that does not contradict to equations (1) and (2). It is worth to emphasize that we discuss conditions of metal penetration into glass capillary, in case of poor degree of moistening and adhesion between them. Increase of casting rate of micro- and nanowires is limited by viscosity of glass η_g and metal η_m, and microwire diameter itself. In case of too poor viscosity of any of components, slippage of metal or glass layers on a border between them may takes place.

Fig.1 shows dependencies of minimal diameter $d=2r$ on a number of parameters of core-formative material and rate of capillary drawing v_s. Hands-on experience shows, that minimal diameters of obtained micro- and nanowires are easily achieved in case of metals with greater adhesive to glass, since in that case metal penetration into a capillary is facilitated as well as its acceleration up to required speed v_s, which can be even greater.

Thus, in order to produce cast nanowires with minimal cross-section, both core and coating thickness, proper selection of glass-metal couple is required, which ensure minimal inter-phase tension between glass and melted metal in a microbath.

Usually such a selection allows to achieve inter-phase tension (at temperature of casting) about 0.5…0.7 of surface tension σ_m of such a melted metal in vacuum. Quantitative assessment of typical casting process (and microbath dimensions) provides r about a couple of microns for many materials at casting rate up to 5 m/sec. E.g., in case of **Bi** estimated value of initial minimal microwire core diameter $d_i = 2r = 3.5$ μm.

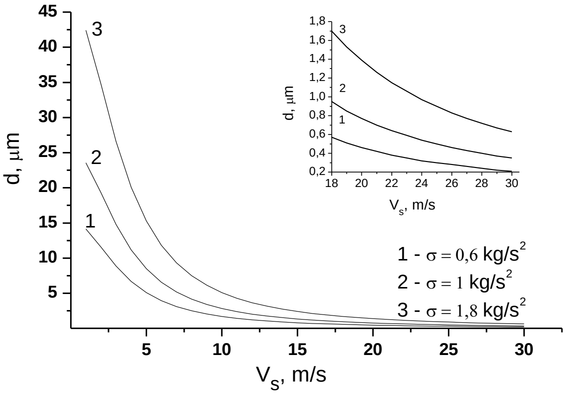

Fig 1. Dependence of minimum of core diameter on stretching speed for different surface tension values.

However, after the melt entered the capillary and during the continuation of the process of nanowire drawing, the condition of further joint flow of the glass capillary with the melt inside changes, and the reduction of the thread diameter becomes possible. If the melt mass in the microbath does not exceed the critical mass, the geometric parameters of the drawn micro- and nanowires depend mainly on properties of the glass tube (its geometry, viscosity, and surface tension) and main parameters of the technological process (speed of capillary drawing, strength of an electromagnetic field of the inductor, micro-bath temperature, and speed of the tube feeding). In that case, in accordance with formula (2), reduction of core diameter of micro- and nanowire is possible, e.g. at increase of speed and tempearture of microbath. It is worth to mention that such a reduction starts from some initial diameter of stretching cone, a core-formative material has already penetrated in.

Therefore, the geometry of the primary and secondary stretching cones has priority for nanowire formation. According to the formula (5) increasing the height of melt drops in microbath (usually H is comparable to the drop diameter $2R_0$) capillary diameter, suitable for entry the metal into it must also decrease. But in case if magnitude of γmgH is much less that $\gamma m v_s^2$ its impact is small in this process. The value of H is critical to the shape of the drop and the diameter of the secondary stretching cone, which in turn determine the diameter of the drawn out glass capillary and the microwire thread after entering of metal in the capillary.

The calculations executed in [9] according to formula (3) have been carried out at a relation of parameters, specific for typical casting process of a resistive microwire. For example, it was assumed that the length of the primary stretching cone L is comparable with the dimensions of metal drop ($L \sim H$). The new calculations made for the conditions of small values of $L < 2H$, showed that in this case the radius of the stretching cone significantly decrease (see fig.2) which should ensure ceteris paribus decrease in diameter of microwire thread cast to nanometric dimensions.

To reduce the length of L, it is proposed to reduce the height of the melt drop. In this case, the pressures of the melt on the critical zone of inflection glass surface microbath also sharply decrease (fig. 3).

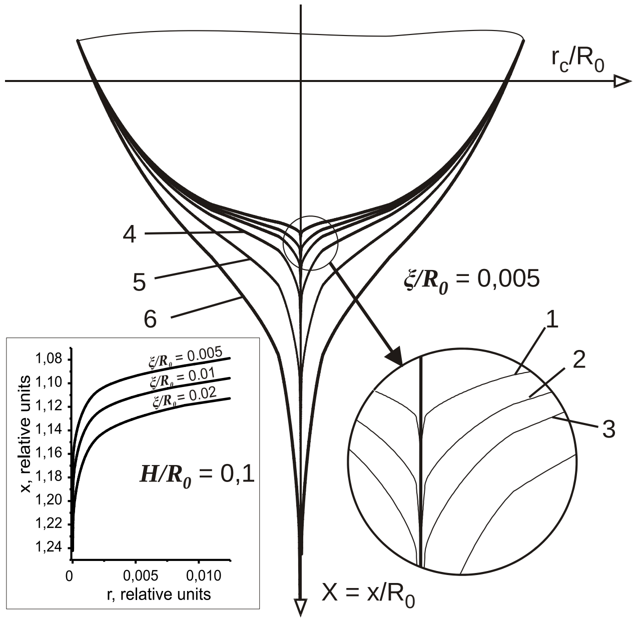

Fig 2. Influence parameters H and ξ on drop shape.

Values of H/R_0: 1 – 0,1; 2 – 0,2; 3 – 0,03; 4 – 0,5; 5 – 1; 6 – 2.

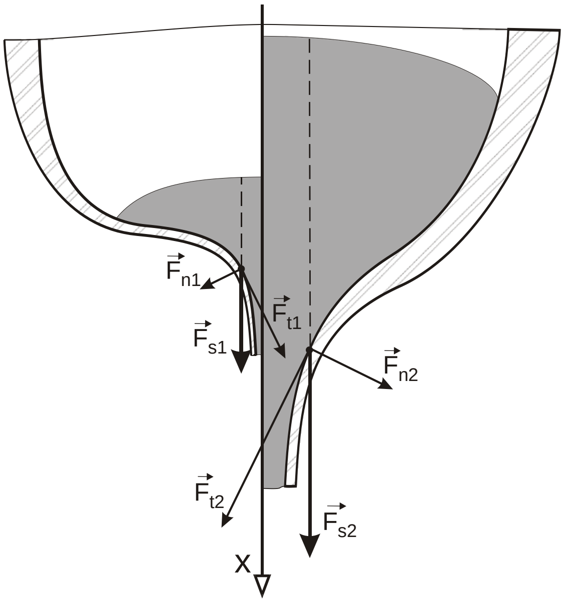

Fig.3. Influence of a melt pressure force on the shape of a primary stretching cone (for the small drop – on the left, for the big drop – on the right).

Correspondingly, the normal component of this force to the surface of the glass envelope of the primary stretching cone is reduced, the diameter throughout its length decreases. This provides a reduction of the inner diameter of the drawn out of the capillary and the received microwire thread.

The obtained conclusions were experimentally checked on the existing equipment for casting microwire with a core from pure (the anode) copper. To do this, after the formation of microbath, the metal drop was decreased by so-called

"Reset" 2/3 of its mass to achieve a more flat (i.e., flattened in the vertical direction) of the form microbath.

Then, the capillary extraction process is continued until filling it with metal. The obtained microwire had a diameter of about 200 ... 300 nm (fig. 4) at the drawing rate 4 m/s.

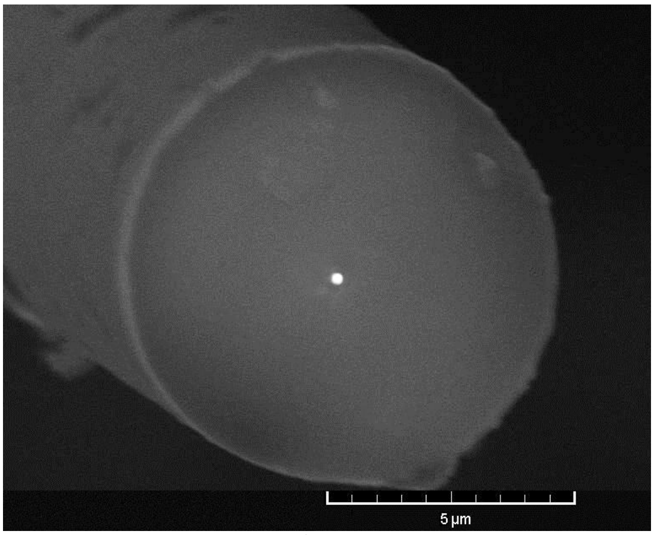

Fig.4. Cross-section of obtained copper microwire.

For further reducing these dimensions and obtaining of nanowires with diameters around 100 nm or less it is necessary to undertake further experiments with other high-frequency inductors: with the larger cone angle, larger diameter and a smaller lower opening.

This is required to form a shallow drop with a sufficiently large amount of metal (not less than 140 mm^3). It is necessary to use also glass pipes with smaller viscosity.

III. CONCLUSION

The carried out analysis and preliminary experiments demonstrated principal potential of production of cast nanowire with nano-core diameter up to 100 nanometers by means of Taylor-Ulitovsky manufacturing method. Improvement of the described technology in combination with selection of compatible materials can ensure further reduction in both core diameter and overall diameter of nanowire.

REFERENCES

[1] Nanotechnologies market: state and prospects. Under general edition ESNL-2008 UMNITS "Sokolinaia Gora". M.MIREA-IKAR, (2008), 100.

[2] E.Badinter, N.Berman, I.Drabenko and others. Cast microwire and its properties, Shtiintsa, Kishinev (1973).

[3] A.Ioisher, I.Nesterovsky. Microwire and devices of resistance, Ed. IX (1972), 25-33.

[4] N.B. Brandt, D.V. Gitsu, A.M. Ioisher, B.P. Kotrubenko, A.A. Nikolaeva. Prib. Tekn. Exp.,3, (1976), 2561.

[5] K..Yu. Arutunov, N.P.Danilova, A.A. Nikolaeva, J.Appl.Phys., p.2, v.76, No 10 (1994), 7139-7141.

[6] R.Zuberek, H.Szymezak, A.Zhukov, M. Vazques and others. J. Magn. Mater. (2007), Vol.316, 890-894.

[7] S.Zotov, K.Kabisov, I.Silkis. Microwire in instrument-making, Ed. IX "Cartea moldoveneasca", Kishinev (1974), 3-17.

[8] E.Badinter, T.Huber, A.Ioisher, A.Nikolaeva, I.Starush. Proceedings of SPIE - Volume 5401. Micro- and Nanoelectronics 2003, K.Valiev, A.Orlikovsky, Editors, May 2004, 257-268.

[9] Yu.Chugaevsky. Microwire and devices of resistance, v. III "Cartea moldoveneasca", Kishinev (1965), 16-26.