PCCP

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

Journal Name

RSCPublishing

COMMUNICATION

Stability and structure of nanowires grown from silver, copper and their alloys by laser ablation into superfluid helium

Cite this: DOI: 10.1039/x0xx00000x

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Eugene Gordon,*[a] Alexander Karabulin,[b] Vladimir Matyushenko,[c] Vyacheslav Sizov[c] and Igor Khodos[d]

Nanowires with 5 nm diameter made of silver, copper, and their alloys were grown in superfluid helium. The silver nanowires being heated to 300K disintegrated into individual clusters. In contrast, copper nanowires were stable at room temperature, and nanowires made of alloys were also stable despite of their low melting temperature.

Based on the results of their experiments on molecular hydrogen condensation in superfluid helium, the authors of ref. 1 and 2 predicted the existence of a specific mechanism for condensation of impurities in superfluid helium induced by their capture in quantized vortices. The particles trapped in the core of the vortex coagulated faster due to collinearity of their velocities; the product of coagulation became longer, and hence its affinity to the vortex core and the lifetime in the captured state both increased resulting in a further increase in the rate of condensation. When the density of vortices is sufficiently high, this mechanism of condensation will prevail over the conventional mechanism controlled by diffusion.[3]

Owing to the one-dimensionality of quantized vortices, the product of such condensation has to be extremely long, thin filament. This process has been proposed to be used for growing metal nanowires.[2] The first experiments have been successful[4,5]: the bundles of thin nanowires were grown by laser ablation of metallic targets immersed in superfluid helium. As was predicted in ref. 2 the nanowire together with its parent vortex tended to pin to the top of the metal rods placed within the condensation zone. It was thus possible to measure the resistance of the nanowires bundle closing the gap between the two electrodes just in a cryostat during its heating, initially in liquid helium and then in helium gas of up to T = 300 K. The morphology and the structure of the bundles precipitated the bottom of the cell were studied at T = 300 K with the TEM microscope. Their morphology was similar for all of the metals studied. The thickness of the nanowires ranged from 7-8 nm for fusible metals[5, 6] to 3 nm for more refractory ones.[4,7] was explained by self-melting of small precursor clusters upon their merging in superfluid helium.[8] Measurements of the resistance of the nanowire bundles closing the electrodes performed in the cryostat at low temperature have shown that the bundles form a web, in which individual wires were interconnected and connected to the electrodes by metallic way[7]. For all metals, the resistance of the nanowires themselves was weakly dependent on temperature up to 300K, being controlled by the scattering of electrons by the surface of the wire rather than by phonons as usual.[9]

Accidently while fortunately, the diameters of the platinum and golden nanowires grown by our technique were close to the diameters of the nanoparticles of these materials, showing abnormally high catalytic activity.[10] Thus it seems promising to use our nanowebs as catalysts. Their possible advantages over commonly used nanocatalysts would be the absence of any support, the possibility of creating and applying high electric fields as well as convenient topology. The performance of our experimental setup allowed to grow up the nanowebs with the total surface up to 10 cm^2. This size is sufficient to determine the characteristics of the chemical reactions they catalyzed by methods of physical chemistry.[9]

The goal of the present work was to produce a stable at room temperature nanoweb made of such a promising for nanocatalysis metal as silver. It turned out to be surprisingly difficult task due to unexpectedly low thermal stability of thin silver nanowires.

Recently, several papers devoted to silver condensation in superfluid helium have appeared. In ref. 11, using experimental approach similar to ours, the authors observed acceleration of the process of silver and copper atom condensation under the liquid helium transition from its normal to the superfluid state; however the monitoring of the coagulation product structure was not carried out. In two other papers, the condensation of silver atoms trapped in the cold helium droplets was observed.[12,13] For this purpose, the sediments heated up to 300 K were studied by using a TEM microscope on a grid placed into a stream of droplets. In large drops where quantized vortex could steadily exist, alignment of the deposited silver clusters along some smooth curves was observed. In ref. 12 the authors found «elongated track-shaped deposits». In ref. 13, TEM photographs demonstrated clearly visible «chains of Ag nanorods». Being unable to observe the primary condensation products the authors of[12] nevertheless came to the conclusion that «segmented Ag chains are shown to be an intrinsic feature of Ag aggregation in helium droplets in the presence of a quantized vortex». Our preliminary experiments on the silver condensation in superfluid helium showed that the rate of the silver nanowire production estimated by the growth of conductivity between the adjacent electrodes was the same as that for other metals. Moreover, after 20 min-long laser ablation the bundles of the silver nanowires grown between the tops of the electrodes became visible to the eye.

However, the TEM images of the sediment instead of wires demonstrated already the same chains of the Ag nanorods as in[13]. We failed to find any works directly focused on the study of the stability of nanowires. The accepted opinion is that the change in the nanowire shape is caused by its melting, which for nanoobjects starts earlier than for the bulk metal. There are few formulas[14] describing the dependence of the melting temperature on the size of the nano-objects with different dimensions, which are in good agreement with the experiment for nanoparticles and nanofilms. According to these formulas, for nanowire with 3 nm diameter the lowering of melting temperature does not exceed 15%. So the low thermal stability of silver nanowires was a surprise to us.

In order to enhance the nanoweb stability, we decided to use silver alloys with copper because the last form quite stable nanowebs.[15] Because copper in its alloys with silver is known[16] to move to the surface of nanoparticles, one would expect sharp decrease in the atom mobility along the surface, and hence increase in the stability of nanowires. Moreover, the presence of copper on the surface of copper-doped silver nanocatalysts causes the increase of their catalytic activity, in particular in epoxidation reactions of ethylene.[17]

The experimental setup was described elsewhere.[5] The metal atoms were introduced in superfluid helium by means of ablation of immersed in HeII metal targets by focused beam of the low-power pulsed laser. The number of metal atoms embedded into liquid per laser pulse was about 10^{12}. The nanowires formed under metal coagulation were partially pinned to the tops of the electrodes placed nearby and partly were deposited onto the carbon-coated copper grids located at the bottom of the cell. Variations of the repetition rate of laser pulses from 500 to 4000 Hz did not affect the morphology and the structure of the nanowire bundles. This means that the nanowire growth takes place between two successive laser pulses, i.e.

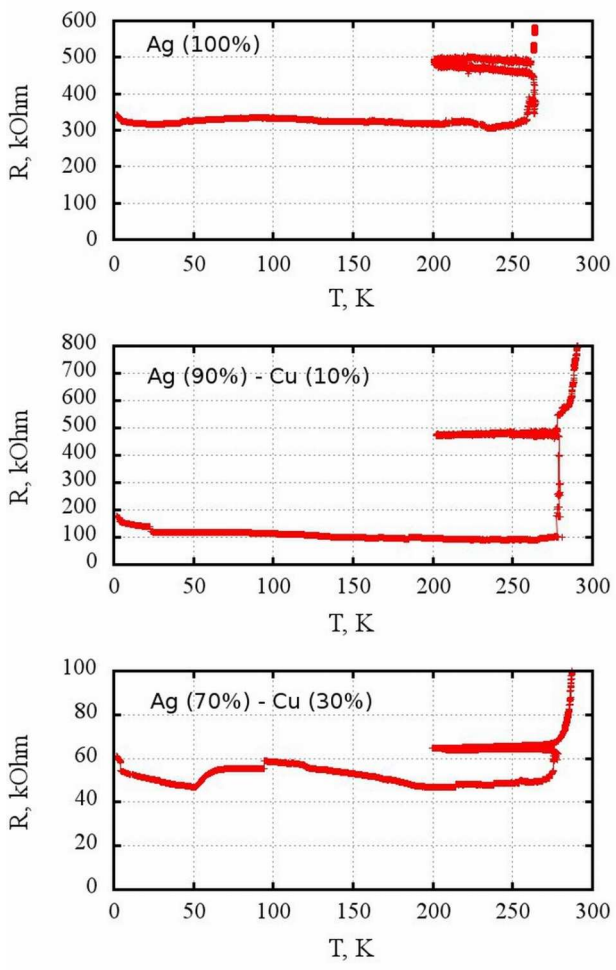

Fig.1. Effective resistance of 1.4 mm long nanowebs made of pure silver and Ag:Cu = 90:10 and 70:30 alloys on helium gas temperature. Gas in the cryostat was slowly (during about 10 hours) warming up; when the apparent resistivity began to rise sharply, the cryostat jacket was filled with liquid nitrogen, and the gas temperature started slowly (during about 4 hours) falling down; then nitrogen was removed and, as a consequence, self-heating renewed. The corresponding reversible resistance changes reflect the actual dependence of the nanowire conductivity on T.[7]

during the time of less than 0.25 ms. Typical times of nanoweb specimen accumulation ranged from 2 to 20 min.

In addition to chemically pure silver and copper their alloys with weight composition Ag:Cu = 90:10 and 70:30 were used as target materials. The first alloy corresponds to the upper limit of the existence of the solid solution (the so-called α-phase), it was prepared by slow sintering of metals at temperature 980°C using borax as flux. The second one has the composition close to the eutectics, it was prepared by rapid cooling of the melting pot initially heated above the melting temperature of both metals. In this case, the size of the individual component crystallites was less than one micron.[18]

The nanowires were growing with approximately the same efficiency as from pure silver and copper as from their alloys. The nanoweb pass-through electrical conductivity was measured directly in the cryostat, the results are shown in Fig.1. The resistance of thin nanowires, at least up to the ambient temperature, is controlled by electron scattering at the wire surface, and thus it does not depend on

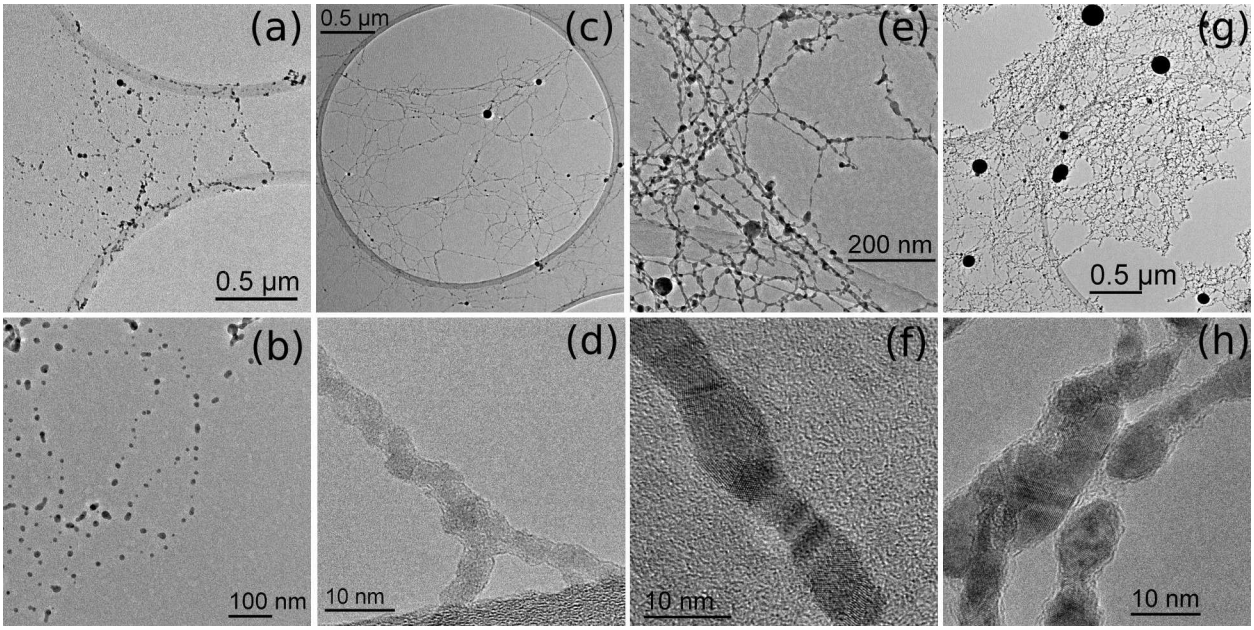

Fig.2. Morphology and structure of sediments on graphite coated copper grid under laser ablation in superfluid helium of various targets: (a) and (b) - silver; (c) and (d) - copper; (e), (f) and (g), (h) - Ag: Cu = 90:10 and 70:30 alloys, respectively. Light halo around the nanowires corresponds to copper oxide formed during the contact with air. The diameter of holes in grid are 2 μm.

temperature.[9] As shown in ref. 9, the sharp increase in the effective resistance observed for all investigated metals at temperatures over 260 K s is associated with breakage of individual nanowires induced by their shortening due to beads appearance under increase of temperature. The annealing at certain temperature T_{an} eliminated this effect for temperatures $T < T_{an}$. The finite independent on T resistance of the annealed silver web demonstrated by the upper curve in Fig.1 proves that it still remains a cross-linked bundle of silver nanowires up to the temperatures close to 300 K.

For the TEM studies, we used the common carbon-coated copper grids with regularly spaced ∅2μ holes (their edges are clearly visible in Fig. 2 a, c, e, and g). The nanowires were both settled on the grid surface and spanned across the holes. The latter wires were the reliable witnesses of the web stability, because even a partial violation of the web integrity would lead to its sinking into a hole and disappearing. The nanowires stabilized on the grid surface under the above partial loss of stability were still quite long. Under the complete loss of stability the nanowires settled on the grid surface decayed into dotted lines of clusters; the metal wetting to the carbon surface could play some role in this process. As seen in Fig.2 (c-d) the copper nanowires retain their integrity despite the significant oxidation of their surface while the sample contacts the air, and the bundles overlap the holes in grid. In contrast, the silver nanowires, collapsed into the "dotted lines" of spherical droplets with no oxidized surface (see Fig.2(a-b)). Naturally, in this case the web spanning across the holes is absent. However, if the TEM analysis of the silver specimen was performed immediately after cryostat warming up, the bean-like silver nanowires were observed on the grid and even across the holes but only for a few hours. The average diameter of these nanowires was about 5 nm, being close to the diameter of copper nanowires, see Fig.2 (b).

As seen in Fig.2, addition of copper to silver, improves the thermal stability of the alloy nanowires. It is seen in Fig.2 (e) and (g) that while the bundles of alloy nanowires contain more breaks of individual wires than the copper nanowires they still form a cross-linked web and they are present in the grid holes. Even with a small (10%) content of copper in silver nanowire, a few atomic layers on surface were found to be oxidized. This effect is consistent with the conclusion of ref. 16 about strong enrichment of the surface layers of Ag:Cu = 97.5:2.5 alloy nanoparticles by copper atoms and their rapid further oxidation. The high resolution images of Ag:Cu nanowires shown in Fig.2 (f) and (g) demonstrate well-expressed interference structure which indicates crystalline ordering. For the 90:10 alloy forming a solid solution (α-phase), this result is not unexpected. However, for the quasi-eutectic 30:70 alloy, the solidification should be followed by phase separation into solid solutions rich in silver (α-phase) and copper (β-phase). Therefore, it is natural to interpret the structure of the quasi-eutectic alloy nanowires shown in Fig.2 (h) as alternating crystalline regions rich in silver and copper. In principle, this is possible because, according to the accepted scenario, the nanoclusters sticking into a nanowire are initially in the molten state.

Anyway, the silver-copper nanoweb can be recommended for the use as nanocatalyst for several chemical reactions.

The data of this study and their comparison with the results of our previous works lead to the following conclusions:

1. Nanowires made of fusible and ductile metal, primarily indium melted at 157°C, are stable at T = 20°C whereas the nanowires made of silver with melting point of 960°C do not survive heating to room temperature. The possible reasons for such behaviour would be rather large difference in wire diameters, 8 nm for In and 5 nm for Ag.
2. The nanowires made of the Ag:Cu alloys show quite different behaviour. While their diameters are basically the same as of silver wires, they exist at 300 K despite the alloy melting temperatures are appreciably lower than that of silver, being equal to 890 and 780°C for Ag:Cu = 90:10 and 70:30, respectively.

Here, it is necessary to look for another cause of stability, which can be associated, for example, with the replacement of mobile silver atoms by immobilized copper atoms at the surface.

3. Being heated to about 260 K, approximately the same temperature for different metals, the nanowires experienced a monotonous reduction in the length, which resulted in their breaking and diminishing the percolation in the web. Interestingly, this led to annealing, i.e. stabilization of the conductivity for any temperature variations below the annealing temperature. In other words, the shape of the nanowires was determined by the temperature at which they were annealed.[9]
4. We do not know the primary shape of our nanowires, but at room temperature, in many cases, regardless of the method of their production, the nanowires had beanlike shapes. It seems that the temperature-induced shape evolution consisted in overflow of the metal atoms from the regions of constrictions to antinodes. At least, such transformation were observed for gold nanowires under their heating in a TEM chamber: at a certain temperature, they decayed into a chain of "fox tracks", precisely as the silver nanowires did at room temperature.
5. Indeed, the cylindrical shape may not be stably for wires few nanometers thick where a significant fraction of atoms belonged to a surface and the surface tension gives a main contribution to the wire energy. The surface tension of silver nanowires was experimentally found to progressively increase with decreasing their diameter below 50 nm and at 30 nm it is twice as large as for the bulk.[19] If this trend continues down to few nanometers in diameter the beanlike shape may have the energy well below the cylindrical one.
6. The situation for the alloy nanowires is even more peculiar. Obviously, the phase diagram at the surface is different from that in the bulk. The reported enrichment of surface by copper atoms in the nanoparticles made of the Ag:Cu = 97.5:2.5 alloy, which is located deep in the region of existence of the solid solution (α-phase)[15], is a direct demonstration of this phenmenon. Therefore, along with formation of the beads, generation of the nanowires consisting of alternating sections of phases rich in one or another component of the alloy can be realized.
7. It is worth to note that we consider the process of changing the shape and the composition at temperatures more than two times lower than the melting temperature. Indeed, what we observe is not melting; rather, it is replacement of atoms that belong to the surface (where the motion requires less energy) within the distances of a few lattice constants.

This work confirms our previous conclusion[3-9] that the coagulation of metals in the superfluid helium containing vortices always leads to the formation of nanowires. The results of refs. 12 and 13 do not contradict to this statement. Indeed, if one accepts their reasoning that the silver condensation products are unbound metal clusters aligned along the vortex core, then it is difficult to explain how their orientation is preserved during the boiling and evaporating of the liquid helium drop deposited on the grid, which no longer contain quantized vortices. Moreover in the recent paper[20] the authors of ref.13 claimed they «exploit the use of quantized vortices to guide the formation of ultrathin nanowires» and that the formation of nanowires «is a general phenomenon».

Authors of ref. 13 pay great attention to the experiment, in which after the capture of silver the helium droplet flow passed through silicon gas target. They concluded that the silicon in the vortex was embedded between silver clusters that repelled each other in the core. Most likely, the explanation is simpler. Two wires were grown in the droplet consistently, silver and silicon ones. Naturally, they were woven together like the wires grown under different laser pulses in our experiments. Upon heating up to room temperature, the silver wire broke into the fragments that stick to silicon filament preserved its integrity. Such a structure observed by the reflective microscope looks like alternating dense fragments of silver and translucent ones of silicon.

Conclusions

The aim of the present work was to produce the silver nanoweb suitable for studies of nanocatalytic processes using our method based on the coagulation of metals in superfluid helium. This objective was achieved. While performing the study we observed interesting effects determining the stability of thin nanowires made of different metals: some of them perished just below their melting point, others decayed already at much lower temperature. Their specificity is not associated with the unjustified use of the concepts introduced in the continuum mechanics for describing the ensembles containing a relatively small number of atoms. Our data confirm the conclusion of Ref. 21 about the appearance of fundamentally new physical and chemical properties at the nanoscale.

Acknowledgements

This work was partially supported by the Russian Foundation for Basic Research, Project #13-03-00788.

Notes and references

[a] Institute of Problems of Chemical Physics RAS, 1 Semenov avenue, 142432, Chernogolovka, Moscow Region, Russia; E-mail: gordon@ficp.ac.ru
[b] National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 31 Kashirskoe highway, 115409, Moscow, Russia; E-mail: avkarabulin@gmail.com
[c] The Branch of Talrose Institute for Energy Problems of Chemical Physics RAS, 1/10 Semenov avenue, 142432, Chernogolovka, Moscow Region, Russia.
[d] Institute of Microelectronics Technology and High Purity Materials RAS, 6 Institutskaya Street, 142432, Chernogolovka, Moscow Region, Russia.

References

1. E.B. Gordon, R. Nishida, R. Nomura, Y. Okuda, *JETP Letters*, 2007, **85**, 581.
2. E.B. Gordon, Y. Okuda, *Low Temp. Phys.*, 2009, **35**, 209.
3. E.B. Gordon, A.V. Karabulin, V.I. Matyushenko, V.D. Sizov, I.I. Khodos, *Chem. Phys. Lett.* 2012, **519–520**, 64.
4. P. Moroshkin, V. Lebedev, B. Grobety, C. Neururer, E.B. Gordon, A. Weis, *EPL*, 2010, **90**, 34002.
5. E.B. Gordon, A.V. Karabulin, V.I. Matyushenko, V.D. Sizov, I.I. Khodos, *Low Temp. Phys.*, 2010, **36**, 590.

6. E.B. Gordon, A.V. Karabulin, V.I. Matyushenko, V.D. Sizov, I.I. Khodos, *Appl. Phys. Lett.*, 2012, **101**, 052605.
7. E.B. Gordon, A.V. Karabulin, A.A. Morozov, V.I. Matyushenko, V. D. Sizov, I. I. Khodos, *J. Phys. Chem. Lett.*, 2014, **5**, 1072.
8. E.B. Gordon, A.V. Karabulin, V.I. Matyushenko, V.D. Sizov, I.I. Khodos, *JETP*, 2011, **112**, 1061.
9. E.B. Gordon, A.V. Karabulin, V.I. Matyushenko, V.D. Sizov, I.I. Khodos, *J. Low. Temp. Phys.*, 2013, **172**, 94.
10. A.T. Bell, *Science*, 2003, **299**, 1688.
11. E. Popov, M. Mammetkuliyev, J. Eloranta, J. Chem. Phys. 2013, **138**, 204307.
12. F. Gomez, E. Loginov, A. Vilesov, *Phys. Rev. Lett.*, 2012, **108**, 155302.
13. D. Spence, E. Latimer, C. Feng, A. Boatwright, A.M. Ellis, S. Yang, *Phys.Chem.Chem.Phys.*, 2014, **16**, 6903.
14. W.H. Qi, *Physica B,* 2005, **368**, 46.
15. V. Lebedev, P. Moroshkin, B. Grobety, E.B. Gordon, A. Weis *J. Low*. Temp. Phys., 2011, **165**, 166.
16. S. Piccinin, S. Zafeiratos, C. Stampfl, T.W. Hansen, M. Havecker, D. Teschner, V.I. Bukhtiyarov, F. Girgsdies, A. Knop-Gericke, R. Schlogl, M. Scheffler, *PRL*, 2010, **104**, 035503.
17. N.L. Nguyen, S. de Gironcoli, S. Piccinin, *J. Chem. Phys.*, 2013, **138**, 184707.
18. D.C. Jenkinson, L.M. Hogan, *J. Crystal Growth*, 1975, **28**, 171.
19. S. Cuenot, C. Fretigny, S. Demoustier-Champagne, B. Nysten, *Phys. Rev B*, 2004, **69**, 165410.
20. E. Latimer, D. Spence, C. Feng, A. Boatwright, A. M. Ellis, S. Yang, *Nano Lett*. 2014, **14**, 2902.
21. R.C. Cammarata, *Prog. Surf. Sci.,* 1994, **46**, 1.