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GROWTH OF SOLID AND HOLLOW NANOWHISKERS FROM NANOSCALE POWDERS

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ABSTRACT

The fast mass growth of solid and hollow nanowhiskers of MoO_3 and WO_3 is obtained owing to the heating of the nanoscale powders of these materials by means of electron beam. Based on our transmission electron microscopic observation the growth mechanism of the MoO_3 and WO_3 nanowhiskers is proposed.

INTRODUCTION

Nanosize materials, because of their unique physical-chemical properties, have gained more importance in modern investigations [1, 2]. One of the most significant problems is to study the influence of external impact, in particular of electron irradiation, on the nanosize materials. In this connection it is necessary to mention the crystallization of amorphous materials [3], the growth of the whiskers of diamond in the chamber of electron microscope [4], the formation of the carbon onions by the electron irradiation [5-10]. The aim of this work is to obtain the MoO_3 and WO_3 solid and hollow nanowhiskers growth under the electron irradiation in the chamber of the electron microscope, as well as the study of the dynamic processes in these nanowhiskers under the influence of the electron irradiation.

EXPERIMENTAL

The investigations were carried out on the transmission electron microscope (TEM) TESLA BS 500 at accelerating voltage of 90kV. To prepare specimens, 1-2 drops of MoO_3 or WO_3 powders suspension in hexane were drifted on the copper grid with carbon coat. For the investigation, both ordinary and treated by vibrationally excited molecules of hydrogen [11-13] the MoO_3 and WO_3 powders were used.

RESULTS AND DISCUSSION

The transmission electron microscopic investigation showed that nanosize MoO_3 and WO_3 powders are the agglomerates of the nanoparticles (size of agglomerates is 0.4-16 μm). If the intensity of electron beam is low, the agglomerates of the MoO_3 and WO_3 nanoparticles remain stable. During the intense irradiation of the MoO_3 and WO_3 nanoparticles agglomerates, irrespective of their method of obtaining, we observed a fast mass formation of nanowhiskers of those materials (Fig.1). As seen from this micrograph, the nanowhiskers of WO_3 can grow separately with an arbitrary orientation as well as with formation of closely packed blocks of nanowhiskers with the same crystalline orientation. Minimal width of MoO_3 and WO_3 nanowhiskers is 8 nm, and the maximal length is 1 μm. Besides common, i.e. solid nanowhiskers, we also observed MoO_3 and WO_3 hollow nanowhiskers. The nanowhiskers of MoO_3 are shown in Fig. 2. The hollow nanowhiskers are indicated by arrows. The analysis of the electron diffraction patterns shows that in both cases they are growing in the direction of [001]. Such coincidence of the growth directions of MoO_3 and WO_3 nanowhiskers is caused by the well known proximity of their crystalline structure [14].

Fig. 1. Closely packed blocks of the same crystalline orientation nanowhiskers of WO_3.

We know three inorganic materials which form low-dimensional tube-type crystals: carbon nanotubes [15], graphite polyhedral crystals [16], cylindrical crystals of serpantine [17], hollow whiskers of aluminium borates [18]. The results of the present work allows to confirm that the nanosize powders of MoO_3 and WO_3 also refer to the above-mentioned list of materials.

As the growth of MoO_3 and WO_3 nanowhiskers passes instantaneously, it is very difficult to follow this process. The TEM investigations show that the nanowhiskers are formed on those parts where a lot of nanoparticles had been. It is seen from Fig. 3, that on the parts with a great number of long nanowhiskers, before their formation there was also a great surface density of nanoparticles. As seen from Fig. 3, by reducing the nanoparticles density (along the border of the carbon coat and on the carbon coat itself) the number and the length of the formed nanowhiskers are also reduced. Our observation revealed that when there are few nanoparticles, the nanowhiskers are not formed. Nanowhiskers can grow on the carbon coat as well as can grow aside where a carbon coat is missing, which is distinctly seen in Fig. 3.

Fig. 2. The solid and hollow nanowhiskers of MoO_3.

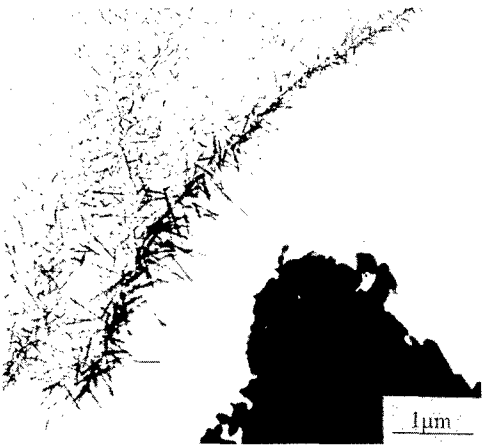

Fig. 3. Dependence of WO_3 nanowhiskers number and length on surface density of nanoparticles.

During the further continuous (~1min) and more intense electron irradiation, a reverse process takes place – the MoO_3 and WO_3 nanowhiskers are gradually destroyed. This destruction passes slower, than the growth of the nanowhiskers was, that allows us to have corresponding micrographs. The WO_3 nanowhiskers on the carbon coat are shown in Fig. 4. The nanowhiskers are in the early stage of destruction under the influence of the electron irradiation. In Fig. 5, the WO_3 nanowhiskers are already in a later stage of destruction. Inside the destroyed nanowhiskers separate nanoparticles obtained by the split and destruction of the initial nanowhiskers under the influence of electron irradiation are distinctly seen. The microdiffraction pattern, obtained from destroyed the MoO_3 and WO_3 nanowhiskers indicates its polycrystalline structure, in the case, that before the destruction the nanowhiskers had been single-crystalline. During the further irradiation with more intense electron beam nanowhiskers are finally destroyed and folded into clew.

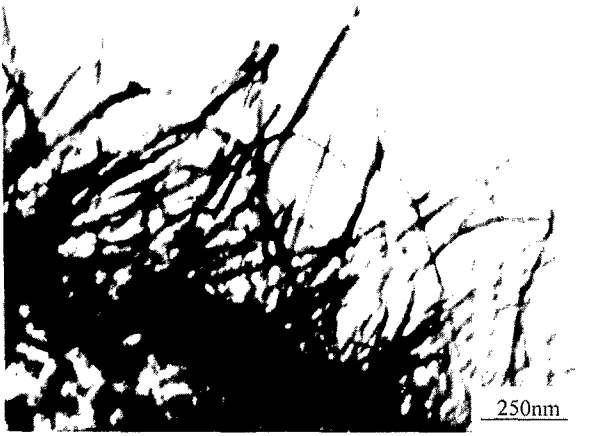

Fig. 4. The WO_3 nanowhiskers in the early stage of destruction.

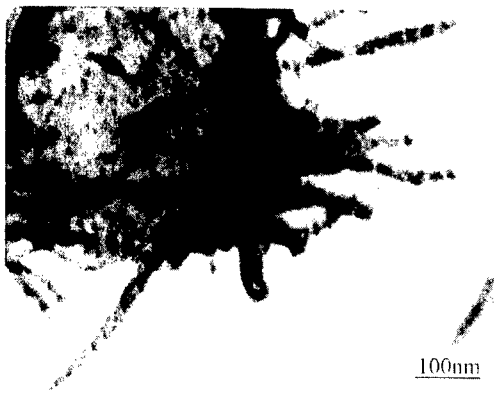

Fig. 5. The WO_3 nanowhiskers in the later stage of destruction.

Based on our TEM investigations, we can propose the following mechanism of the growth of MoO_3 and WO_3 nanowhiskers. In the first stage it is necessary to have individual (isolated from each other) nanoparticles, which are as a crystalline nuclei for the growth of the nanowhiskers. Next, under the influence of the electron beam by heating [19] the molecules of the MoO_3 and WO_3 from those nanoparticles are generated. As a result of a thermal movement and surface diffusion the uninterrupted migration of MoO_3 and WO_3 molecules on the carbon coat or on the agglomerate takes place. The diffused molecules interacting with a crystalline nuclei with [001] orientation, which corresponds to the maximal rate of the growth, form MoO_3 and WO_3 nanowhiskers. If the MoO_3 and WO_3 nanowhiskers grow on the borders where the carbon coat is broken or on the edges of agglomerates in aside where carbon coat is absent, diffusion of the molecules takes place on the surface of the already formed part of the nanowhiskers. Taking into account the high rate of the surface diffusion of the molecules, in our case generated by heating during the electron irradiation of isolated from each other nanoparticles, the almost instantaneous growth of the MoO_3 and WO_3 nanowhiskers becomes clear. This growth is stopped when the quantity of the individual nanoparticles is reduced. When hollow nanowhiskers are formed, it is evident that the initial crystalline nucleus has a circle-like form which is caused by the topology of a part where the given nucleus was formed. As a result, the same process as at the growth of solid nanowhiskers a further growth of hollow nanowhiskers takes place.

CONCLUSION

At the presence of MoO_3 and WO_3 nanoparticles of definite density, irrespective of the method of their obtaining, under the influence of an intense electron irradiation owing to heating, solid and hollow MoO_3 and WO_3 nanowhiskers are grown. The formation of the hollow nanowhiskers testifies the surface nature of their growth.

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REFERENCES

1. Metastable Phases and Microstructures, edited by R.Bormann, G.Mazzone, R.D.Shull, R.S.Averbakh and R.F.Ziolo (Mater. Res. Soc. Proc. **400,** Pittsburgh, PA, 1995) p. 368.
2. Nanophase Materials, 1994. edited by G.S. Hadjypanais and R.W.Siegel (Kluwer Academic Publishers, Dordrecht/ Boston/ London, 1994), p.808.
3. G.Schimmel, Elektronenmikroskopische Methodik, (Springer-Verlag, Berlin, Heidelberg, New York, 1969) p.250.
4. V.D. Zamojskii, and A.N.Lousin, , Dokl. AN SSSR, **224,** 369 (1975).
5. D Ugarte, Nature (London), **359**, 707 (1992).
6. W.A. de Heer and D.Ugarte, Chem.Phys. Lett., **207**, 480 (1993).
7. K.G.Mckay, H.W. Kroto and D.I.Wales, I.Chem. Soc. Faradey Trans. **88**, 2815 (1992).
8. Q.Ru, M.Okamoto, Y. Kondo and Takayanagi, Chem.Phys. Lett. **259**, 425 (1996).
9. B.S. Xu and S-I.Tanaka, Proc. Annu..Meeting Scan. Soc. Electron Microsc., **49**, 434 (1997).
10. T.Oku, T. Hirano and K.Suganuma, J. Mater. Res. **14**, 4266 (1999).
11. R.T Malkhasyan, in Metastable Phases and Microstructures, edited by R.Bormann, G.Mazzone, R.D.Shull, R.S.Averbakh and R.F.Ziolo (Mater. Res. Soc. Proc. **400,** Pittsburgh, PA, 1995)pp. 77 – 82.
12. R.T. Malkhasyan and G.H . Movsesyan, Pribory Techn. Exper. **4**, 127 (1991).
13. R.T. Malkhasyan, G.H. Movsesyan and V.K Potapov, Khim. Vysok. Energii. **26**, 63 (1992).
14. K.Schubert, Kristallstrukruren Zweikomponentiger Phase, (Springer-Verlag, Berlin, Gottingen, Heidelberg. 1964), p. 485.
15. S.Iijima, Nature, **354**, 56 (1991).
16. Y.Gogotsi, I.A. Libera, N. Kalashnikov and M.Yoshimura, Science. **290**,317 (2000).
17. E.I.W.Wittaker, Acta Cryst. **21**, 461 (19660).
18. Y.Gogotsi, V. Yaroshenko and F.Porz, J.Mater. Sci., Lett., **11**, 308 (1992).
19. L.W.Hobbs, in Introduction to Analytical Electron Microscopy, edited by Hren et al. (Plenum, N.Y.1997) p.437- 450.