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Production And Application Advanced W-based Nanopowders

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1. ABSTRACT

Low agglomerated tungsten disulfide nanoparticles with mean diameter in range of 20 – 80 nm have been successfully produced by aerosol synthesis method. The particles size was changed by process parameters. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM). Onion-like structures with interlayer distance of 0.6363 nm was obtained. Polyimide-based composites materials filled by WS₂ nanoparticles with different content were developed and its tribological properties were studied. The main application areas for prepared material were determined.

2. INTRODUCTION

Chalcogenides of W and Mo well known solid lubricant materials widely used as solid lubricant materials for creation of antifriction coating for loaded parts in such areas as aerospace, nuclear, cryogenics, machine tools, racing engines, cutting tools, die casting, small arms.

Because it works in high vacuum and wide temperature interval is from -460°F to 1200°F (-273°C to 650°C) in normal atmosphere, -350°F to 2400°F (-188°C to 1316°C) at 10⁻¹⁴ Torr.

As additional advantages such materials are non-toxic, corrosion resistant, stability to radioactivity and etc [1-3]. In comparison with oils, greases, silicones, polyphenylethers, perfluoropolyethers, some cryogenic liquids and other traditional lubricants the solid lubricant materials have such quality like practically no tendency to flow, creep or migrate, so they can be relied on to remain in place for long periods. In this way nanoparticles expect best properties for application because it can be deeply impregnated in pores or structure of metallic matrix,

used as a filler for polymer-composite material and make stable suspension with any kinds of liquid media.

Synthesis and application of metallic, composite and ceramic nanoparticles are emerging in wide areas especially in powder metallurgy, electronics and biotechnology.

It developed that the major characteristics of nanoparticles as a size distribution, structure, morphology, surface condition and chemical composition extremely depend from production technology [4-5]. As compared with other methods the chemical synthesis of nanoparticles in the gas phase is a rapidly growing field because of its versatile applicability to almost all materials and high rate of production capability with little agglomeration. Since the properties of these nanoparticles are basically determined by their mean size, size distribution, external shape, internal structure, and chemical composition, the characteristics of powders must be precisely controlled during the production of the nanoparticles [6].

In this paper, we developed synthesis of W-based nanoparticles, such as pure tungsten and tungsten disulphide WS₂ with mean size in range of 8-25 nm and 20-80 nm respectively by chemical vapor condensation method (CVC). The effect of processing parameters and annealing process on the microstructure and size of nanoparticles were investigated.

3. EXPERIMENTAL

3.1 Nanoparticles production

For nanoparticles production improved scheme of chemical vapor condensation method (CVC) Fig. 1, which was adjusted for mass production of nanoparticles, were applied. The general scheme of CVC process was presented previously [8]. To produce pure tungsten nanoparticles, a carrier gas of high purity argon or helium is fed through a heated bubbling unit containing the metalloorganic precursor of tungsten hexacarbonyl ($W(CO)_6$) at the vaporization temperature. Concentration of precursors in gas phase was controlled by gas flow rate, temperatures of evaporation, pressure inside of reactor. Temperatures of reactor were in range of 450-1100°C, and were optimized. Using accelerating gas as well as carrier gas was applied for changing precursor residential time in reaction zone and its concentration of precursor in gas phase.

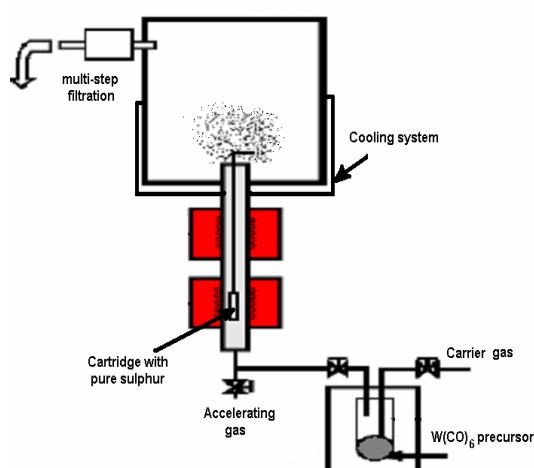


Fig.1. Scheme of (CVC) experimental setup

The gas flow contained precursor vapor passed through the heated tubular reactor to the work chamber. The removable cartridge with crystalline sulphur, which was located inside first zone of reactor, was used as a source of sulphur for WS_2 nanoparticles synthesis. The gas flow inclusive vapor of precursor passed through the both zones of reactor subsequently. In the first zone of reactor the vapor of sulphur mixed carbonyl vapor and then get in second zone of reactor heated to carbonyl pyrolysis conditions as shown on Fig. 1. Hence, precursor decomposition and nanoparticles formation pass in the sulphur contained atmosphere. As a way to produce nanoparticles with exact

chemical composition the excess of sulphur in gas phase was provided.

In order to remove that excess of sulphur as-prepared nanoparticles were heat-treated in the reactor with two interconnected zones in vacuum or inert atmosphere conditions. Free pure sulphur from the powder was evaporated at the temperature of 200°C and condensed in the cold zone at the room temperature.

3.3 Characterization methods

The phase analysis of samples was carried out on Siemens D5000 diffractometer with the use of monochromatic $K\alpha$ copper radiation. ($\lambda=0.154051\text{nm}$). The morphologies and particles size distribution were determined by transmission electron microscopy (TEM) using JEOL JEM-2000FXII equipment. The powder for TEM investigations was ultrasonically dispersed in ethanol and dropped on a carbon coated copper grid. The average particle size of each sample was calculated as the center of gravity of particles size distribution, which was estimated by measuring of diameters of 200-300 nanoparticles from TEM microphotographs.

The friction properties measurements was performed at laboratory atmosphere (~50 % humidity) using a ring-block tester for metal matrix and pin-on disk tester for polymer composite materials.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Synthesis and characterization of nanoparticles by CVC method was described previously [7-9]. Pure tungsten nanoparticles were synthesized by the same way as Fe-based nanoparticles at the reactor temperatures of 600-1100°C and have mean size in the interval of 10-25 nm respectively. Particles did not appear at the temperatures lower than 550°C. In order to produce tungsten disulphide nanoparticles the decomposition of tungsten hexocarbonyl was carried out in the presence of sulphur vapor with the partial pressure of S_2 vapor of 0.02-0.04 atm. In such condition we achieve about ten times excess of pure sulphur in the gas phase.

Fig.2 shows phase composition of products, which can be synthesized in experimental condition as function of experimental parameters, taking in the account that excess of sulphur always exists in product. It is clear that the rate of reaction between W and S₂ in the gas phase increased with the increasing temperature and the region of WS₂ appearance becomes wider.

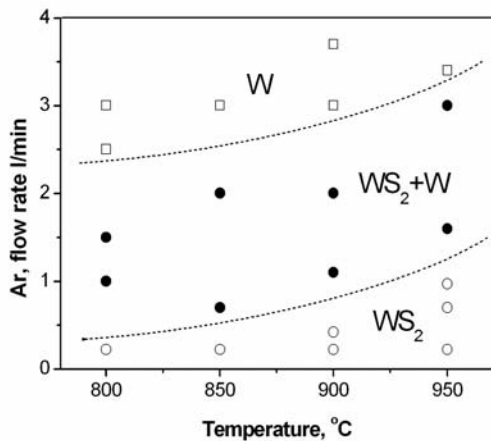


Fig.2. Phase diagram of products

With the Ar carrier gas flow rate increased the residential time of particles in reactor reduced and pure W nanoparticles could be observed. It means that in that case there is no enough time to complete reaction.

Normal and lognormal particles size distribution was evaluated for as-prepared particles, in all cases it seems to be bimodal. With the increase of reaction temperatures, the average size of particles increases insignificantly and the particle size distribution becomes wider and more asymmetrical with the size increment. Some agglomeration of already formed nanoparticles can be observed. Fig. 3 (a) shows TEM micrographs of tungsten disulphide nanoparticles with the mean size of 25 and 40 nm. Nanoparticles have rounded shape and their TEM image demonstrates so-called onion structure Fig. 3 (b), which consist of concentric layers with the interlayer distance of 0.61058 ± 0.042 nm irrespective of particle size.

X-ray diffraction pattern does not show any additional peaks except peaks WS₂. In order to estimate the lattice parameters and grain size, a matching of X-ray photographs with “released”

reflections intensities was made for samples prepared at the different temperature.

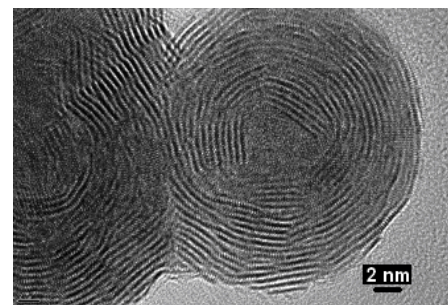
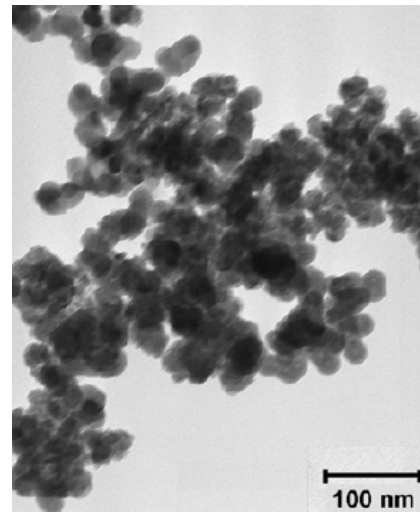


Fig.3. HR TEM images of WS₂ (a, b) nanoparticles

The obtained parameters of the lattice are as follow: $a=0.3162$ nm and $c=1.2726$ nm for the first and $a=0.3208$ nm and $c=1.9104$ nm are for second one. Interlayer distance in „c” direction is equals $c/2$ and $c/3$ respectively for 2H and 3R structures and evaluated as $c_0 = 0.63 \pm 0.01$ nm. It means that distances between the layers are identical for both samples and it is in a good correspondence with microphotograph measurements. Thus it expects that these structures contain foreign atoms intercalated between the S-W-S layers, which cause weakening of the bonds and modification of the crystalline atom structure. The presence of such atoms, creating a sub-structure with weak long-range order, it determined from X-ray diffraction patterns [10].

The friction and wear behavior were studied for the produced WS₂ solid lubricant ultrasonically impregnated in structure of

porous alumina thermo-sprayed coating and for polymer composite material.

Porosity of alumina matrix was estimated as about 3 % and penetration of nanoparticles was provided by ultrasound treatment. It is expected that the spherical nanoparticles of WS₂ may be applied also in the case of denser matrix [11]. The value of wear coefficients for bronze-alumina oxide + nanoparticles were less than 0.08 and low wear rate over under load of 300 N and sliding velocity of 1 m/s, while the friction coefficient of the native piece was about 0.2. It is expected that the slippery nature of the nanoparticles leads to their fast displacement from the pores to the contact area and thus protects the rubbed surfaces.

In second case the polymer composite with nanoparticles content about 5 wt. % were prepared Powder of R-BAPB polymer was mixed with nanoparticles by careful stirring. Further samples were made by cold compacting and than hot compacting at the temperature about 3500C with further cooling under the pressure.

Friction and wear properties was measured at the room temperature in contact with stainless steel Ra 0,07 (IKO Bearings Germany WS81215) with contact pressure 1,0 MPa during of 25 min with test speed 0,3 m/s. As dependence of time the value of friction coefficient was obtained as follows: 0.3972-5 min, 0.4109-15 min, 0.4197-25 min. In contrary, extremely insignificant wear were found in compare with pure polymer matrix or filled by CNT or Astrolen nanofibers.

4. CONCLUSION

The possibility to produce crystalline W and WS₂ nanoparticles with mean size from 20 to 70 nm by gas phase synthesis method was shown. Phase and chemical composition of nanoparticles studied and can be controlled by experimental parameters. The Al₂O₃ thermo-sprayed coating impregnated with WS₂ nanoparticles in couple with bronze exhibited very low friction coefficient and slow wear. Polymer composite with nanoparticles shows at the same time some increasing of friction coefficient and extremely low wear.

Produced powders have relative small particle size with round shape and better friction properties in comparison with commercially available 2H layered WS₂ nanoparticles.

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