

Im Eisenbahntransport gibt die Anwendung der Rückgewinnung den großen Effekt. Die Nutzbremmung ermöglicht es, die Elektroenergie einzusparen und den Verschleiß des Bremsbackens zu verringern. Auf den abgesonderten Grundstücken mit den steilen Abstiegen kann bis zu 20 % elektrischer Energie eingespart werden, die in Belüftungssystemen der Züge verbraucht wird. Wenn der Zug nach dem steilen Abstieg folgt, werden die Lokomotive und der Zug gewöhnlich von den pneumatischen Bremsen periodisch abgedrosselt, damit die zulässige Geschwindigkeit nicht überschritten wird. Daraufhin verringert sich die Geschwindigkeit der Bewegung des Zuges, und wächst dann wieder. Bei der Rekuperationsbremmung kann man auf dem Abstieg die ständige Geschwindigkeit beibehalten, die sich der zulässigen nähert, abhängig vom Zustand der Eisenbahnlinie.

Das System KERS ist eine einzigartige Technologie mit einer großen Zukunft.

LITERATURVERZEICHNIS

1. KERS [elektronische Ressource] URL:<http://www.mercedesamgf1.com>
(Behandlungsdatum 13.03.2015)
2. KERS [elektronische Ressource] URL: <http://autosport.com.ru>
(Behandlungsdatum 13.03.2015)
3. Technisches Reglement [elektronische Ressource] URL: <http://www.formel1.de>
(Behandlungsdatum 14.03.2015)

SYNTHESIS AND PROPERTIES OF NANOSTRUCTURED TUNGSTEN CARBIDE – A REVIEW

K. N. Shatrova, E.Ya. Sokolova
Tomsk Polytechnic University

Introduction

Currently, tungsten carbide plays an important role in technology and manufacture, because it has a number of distinct physical and chemical properties. Tungsten carbide is the superhard tool materials. The features of such materials are high hardness, strength, heat resistance, wear resistance, corrosion resistance. Moreover, tungsten carbide differs from other superhard materials by thermal stability of its mechanical properties [1]. Thanks to these distinctive features, tungsten carbide is widely used in the manufacture of structural materials and tools, that can be used not only under normal conditions, but also at high temperatures, in corrosive media and under heavy loads and tension.

Over the past two decades many attempts of nanopowder synthesis and sintering of tungsten carbide for the bulk sample with a nanocrystalline structure have been made. Superhard bulk ceramic materials based on tungsten carbide with the addition of nickel, cobalt, and tungsten carbide without additives have already been obtained. Their grain size is less than 100 nm. Real interest to the tungsten carbide with the nanocrystalline structure is caused by the potential possibility to improve its mechanical

properties [2-4]. This will increase the service life and reliability of the instruments made from tungsten carbide. By now many methods for tungsten carbide preparation have been proposed including tungsten and graphite powder grinding in a ball mill and complicated chemical synthesis process.

It is known that materials in the nanocrystalline state have a number of unique chemical, electrical, optical, magnetic and other properties that are not common for substance with larger particle sizes. Nanosized tungsten carbide is not an exception. Contemporary literature data suggest the possibility of tungsten carbide application as an alternative to platinum catalysts for hydrogen production and electricity generation in fuel cells [5-9]. It is related to the fact that platinum is a noble and very expensive metal which leads to significant increase of the cost of the whole technological process. Tungsten carbide is less expensive material. A synergistic effect is observed when it is used together with platinum, which results in improving the catalytic activity.

Thus, tungsten carbide in the nanocrystalline state attracts great interest of many scientists and researchers due to the discovery of its new properties.

Currently, there is a wide variety of methods for nanosized tungsten carbide preparation.

Synthesis of nanosized tungsten carbide powder

H. Singh and O.P. Pandey suggest a new method for producing tungsten carbide WC from scheelite ore containing tungsten. The mixture of pre-milled ore, activated charcoal and magnesium in proportions of 1:2:1, was heated in an autoclave up to 800 °C within 20 hours. Undesirable impurities (CaO, MgO and SiO₂) generated during heating were removed by washing firstly with a solution of hydrochloric acid HCl and then with alkaline solution NaOH. The advantages of this method over the traditional ones is the formation of less harmful substances and low cost [10].

Hexagonal tungsten carbide nanoparticles WC synthesized by carburizing tungsten/tungsten oxide (WO₃)/non-stoichiometric tungsten oxide phases (WO_{3-x}) were obtained from a wire explosion process. Carburization was carried out using multi walled carbon nanotubes at temperature of 1250 °C for 7 hours. As a result spherical tungsten carbide particles were obtained and the geometric mean size of these particles is about 19 nm [11].

Tungsten carbide nanopowders were synthesized by electric discharge machining followed by annealing in nitrogen and hydrogen atmospheres. Cubic tungsten carbide phase (WC_{1-x}) was formed during electrical discharge machining. When annealing powder in a nitrogen atmosphere, WC_{1-x} phase is gradually being transformed into hexagonal phase W₂C, and then is completely converted into nanocrystalline hexagonal phase WC at temperature 1200 °C. The WC nanoparticles have a carbon shell. When annealing the cubic tungsten carbide powder in a hydrogen atmosphere, WC_{1-x} phase is transformed into W₂C, then into tungsten at 1000 °C or directly from WC_{1-x} into W [12].

This paper focuses on tungsten carbide nanoparticles preparation by powder grinding in a ball mill twice. After the first milling the average particle size was 168 nm, the particle size distribution was enough narrow. After the second milling the

average particle size decreased to 89 nm, and the particle size distribution was narrower [13].

Microspheres tungsten carbide nanoparticles were prepared from resorcinolformaldehyde polymer and ammonium metatungstate salt containing carbon and tungsten, respectively. These substances were mixed with water, evaporated under 367 K within 24 hours, then dried and heated up to 1173 K in an argon atmosphere. The diameter of the formed sphere-like tungsten carbide nanoparticles was 4.2 microns [14].

Mesoporous structures of tungsten carbide (WC-700-m, WC-800-m, WC-900-m) are formed from layered tungsten nitride nanoparticles at temperatures of 700, 800 and 900 °C in an atmosphere of CH₄ (25%)/H₂ (75%) within 9 hours. Tungsten nitride nanoparticles were prepared by the hydrothermal method. It was discovered that the first sample (WC-700-m) consisted of WC_{1-x} phase, the second sample (WC-800-m) consisted of WC_{1-x}+WC phases, the third sample (WC-900-m) consisted of WC [15].

Nanocrystalline tungsten carbide WC was synthesized by the intermittent microwave heating of specially prepared precursor containing 30% W and 70% C (wt.). It was found that particle sizes do not exceed 50 nm [16].

Nanosized tungsten carbide-cobalt composite powder was synthesized by a thermal plasma, in which the ammonium paratungstate and cobalt oxide reacted with a gas mixture comprising CH₄, H₂ and Ar. During the recovery and carbonization of vaporized precursors nanosized composite powder containing tungsten carbide (WC_{1-x}), cobalt (Co) and a small amount of W₂C and W phase is formed. The particle size of the synthesis tungsten carbide powder was less than 20 nm. The resulting composite powders were subjected to thermal treatment in hydrogen environment for complete carburization of WC_{1-x}, W₂C and W phases to the WC phase, as well as for removing excess carbon. As a result, a nanosized WC-Co composite powder with a particle size less than 100 nm was obtained [17].

There is a unique one-step method for obtaining of nanosized tungsten carbide. The synthesis process was carried out using a high-current pulsed coaxial magnetoplasma accelerator (CMPA) with graphite electrodes, which generated a high speed tungsten-carbon electrodischarged plasma jet [18, 19]. Power was provided by a pulsed accelerator source with a maximum stored energy up to 360 kJ. Tungsten and carbon (soot) precursors in the form of mixed powders were placed in a plasma structure formation zone, accelerated in the coaxial system. According to current and voltage oscillograms and the calculated curves of power the acceleration process lasted up to 500 ms at current amplitude up to 150 kA and discharge power of 150 MW. About 30 kJ of energy was allocated in the accelerating channel of CMPA. The plasma shot was produced in a sealed chamber filled with commercially pure argon under normal pressure and temperature. Opening of the chamber and the collection of the synthesized powder product was carried out after natural intensive cooling and deposition of suspended particles on the reactor walls. As a result, tungsten carbide with an average particle size less than 50 nm was obtained [20, 21]. Synthesized tungsten carbide had high heat resistance.

Sintering of nanocrystalline tungsten carbide ceramics

Binderless tungsten carbide (WC) ceramics was obtained using reactive spark plasma sintering from the powder mixture of tungsten oxide WO_3 , tungsten and carbon black. The ceramics was obtained at 1500 °C and it had high hardness (27.07 GPa) [22].

The following authors A. Gubernat, P. Rutkowski et al. present the results of the studies referring to hot-pressing of submicron WC powders without sintering additives, but with the addition of carbon or tungsten or both elements simultaneously. The aim of the work was to obtain dense single-phase tungsten carbide polycrystalline. Carbon was added to reduce while sintering the amount of tungsten oxide coating tungsten carbide grain. A mixture of carbon, tungsten carbide and tungsten was homogenized by grinding in a ball grinder in ethyl alcohol within 12 hours. After evaporation of alcohol, the mixture is rubbed through a sieve and granulated, to prepare it for hot-pressing. The conditions of the sample hot-pressing were the temperature of 1950-2150 °C and pressure of 25 MPa [23].

The researchers K.-M. Tsai, Ch.-Y. Hsieh and H.-H. Lu analyze tungsten carbide with a small amount of TiC and TiN. The powder was milled in a ball mill, and samples were pre-formed beforehand under temperature of 200 °C and pressure of 130 MPa. The specimens were sintered in a furnace at 1600 °C. Density of sintered specimen was 15.43 g/cm³ their Vickers hardness number was 23.14 GPa and their fracture toughness was 6.56 MPa·m^{1/2} [24].

Titanium carbide ceramics with a small addition of tungsten carbide was obtained by spark plasma sintering at temperature of 1450-1600 °C. The addition of 3,5% WC (wt.) decreased the sintering temperature of ceramics by approximately 150 °C, and degradation of mechanical properties was not observed [25].

Conclusion

Thus, the invention of nanotechnology has led to a “new industrial revolution”. It is due to the fact that nanostructured materials with unique properties can help improve our daily lives. In particular, these materials include nanosized tungsten carbide. Currently, there are dozens of proposed methods for the preparation and synthesis of nanopowders and ceramics from tungsten carbide, as well as composite materials based on it. It is obviously, that practically all methods of nanopowder synthesis except [10, 20] contain at least two stages. It may be noted that the typical stages considered in a number of methods are the production of tungsten oxide with the following carburization to WC, W_2C and WC_{1-x} at temperatures above 600 °C.

Unfortunately, now none of the methods of preparation of nanosized tungsten carbide has received industrial applications. This is due to the fact that the methods of nanosized WC and W_2C synthesis from pure starting reagents W and C make the product expensive. Moreover, the process of synthesis from tungsten and carbon-containing material is a multi-step and time consuming one.

REFERENCES

1. M. Razavi, M.R. Rahimpour, R. Yazdani-Rad. A novel technique for production of nano-crystalline mono tungsten carbide single phase via mechanical alloying. *Journal of Alloys and Compounds*. 2011. № 509. P. 6683-6688.
2. Z.Z. Fang, X. Wang, T. Ryu, K.S. Hwang, H.Y. Sohn. Synthesis, sintering, and mechanical properties of nanocrystalline cemented tungsten carbide – A review. *International Journal of Refractory Metals and Hard Materials*. 2009. № 27. P. 288-299
3. C.-J. Li, G.-J. Yang. Relationships between feedstock structure, particle parameter, coating deposition, microstructure and properties for thermally sprayed conventional and nanostructured WC–Co. *International Journal of Refractory Metals and Hard Materials*. 2013. № 39. P. 2-17.
4. A.S. Kurlov, A.I. Gusev. Phase equilibria in the W–C system and tungsten carbides. *Russian Chemical Reviews*. 2006. № 75. P.617-636.
5. J. Kim, J.-H. Jang, Y.-H. Lee, Y.-U. Kwon. Enhancement of electrocatalytic activity of platinum for hydrogen oxidation reaction by sonochemically synthesized WC_{1-x} nanoparticles. *Journal of Power Sources*. 2009. № 193. P.441–446.
6. M. Perchthaler, T. Ossiander, V. Juhart, J. Mitzel, C. Heinzl, C. Scheu, V. Hacker. Tungsten materials as durable catalyst supports for fuel cell electrodes. *Journal of Power Sources*. 2013. № 243. P. 472-480.
7. Ch. Tang, D. Wang, Zh. Wu, B. Duan. Tungsten carbide hollow microspheres as electrocatalyst and platinum support for hydrogen evolution reaction. *International Journal of Hydrogen energy*. 2015. № 40. P. 3229-3237.
8. V.M. Nikolic, D.L. Zugic, I.M. Perovic, A.B. Saponjic, B.M. Babic, I.A. Pasti, M.P.M. Kaninski. Investigation of tungsten carbide supported Pd or Pt as anode catalysts for PEM fuel cells. *International Journal of Hydrogen Energy*. 2013. № 38. P. 11340-11345.
9. Y. Oh, S.-K. Kim, D.-H. Peck, J.-S. Jang, J. Kim, D.-H. Jung. Improved performance using tungsten carbide/carbon nanofiber based anode catalysts for alkaline direct ethanol fuel cells. *International Journal of hydrogen energy*. 2014. № 39. P. 15907-15912.
10. H. Singh, O.P. Pandey. Single step synthesis of tungsten carbide (C) nanoparticles from scheelite ore. *Ceramics International*. 2013. № 39. P. 6703-6706.
11. S. Aravinth, B. Sankar, M. Kamaraj, S.R. Chakravarthy, R. Sarathi. Synthesis and characterization of hexagonal nano tungsten carbide powder using multi walled carbon nanotubes. *International Journal of Refractory Metals and Hard Materials*. 2012. № 33. P. 53-57.
12. M.-H. Lin. Synthesis of nanophase tungsten carbide by electrical discharge machining. *Ceramics International*. 2005. № 31. P. 1109-1115.

13. H. Meng, Zh. Zhang, F. Zhao, T. Qiu. Preparation of nanoparticles by twice ball milling. *International Journal of Refractory Metals and Hard Materials*. 2013. № 41. P. 191-197.
14. D.J. Ham, R. Ganesan, J.S. Lee. Tungsten carbide microsphere as an electrode for cathodic hydrogen evolution from water. *International Journal of hydrogen energy*. 2008. № 33. P. 6865-6872.
15. A-R. Ko, Y.-W. Lee, J.-S. Moon, S.-B. Han, G. Cao, K.-W. Park. Ordered mesoporous tungsten carbide nanoparticles as non-Pt catalysts for oxygen reduction reaction. *Applied Catalysis A: General*. 2014. № 477. P. 102-108.
16. M. Nie, P.K. Shen, Z. Wei, Q. Li, H. Bi, Ch. Liang. Preparation of pure tungsten carbide and catalytic activity of platinum on a tungsten carbide nanocrystalline support for oxygen reduction. *ECS Electrochemistry Letters*. 2012. № 1. P. 11-13.
17. T. Ryu, H.Y. Sohn, K.S. Hwang, Zh.Z. Fang. Plasma synthesis of tungsten carbide and cobalt nanocomposite powder. *Journal of Alloys and Compounds*. 2009. № 481. P. 274-277.
- A. Sivkov, A. Pak, I. Shanenkov, J. Kolganova, K. Shatrova. Synthesis of ultra dispersed graphite-like structures doped with nitrogen in supersonic carbon plasma flow. *IOP Conference Series: Materials Science and Engineering*. 2014. № 66. P. 1-6.
18. D.Yu. Gerasimov, A.A. Sivkov. Electroerosive wear of the barrel of a coaxial hybrid magneto-plasma accelerator in the acceleration of solids. *Journal of Applied Mechanics and Technical Physics*. 2012. №53. P. 140-146.
- A. Pak, A. Sivkov, I. Shanenkov, I. Rahmatullin, K. Shatrova. Synthesis of ultrafine cubic tungsten carbide in a discharge plasma jet. *International Journal of Refractory Metals and Hard Materials*. 2015. № 48. P. 51-55.
19. A.A. Sivkov, A.Y. Pak, I.A. Rakhmatullin, K.N. Shatrova. Production of ultrafine tungsten carbide in a discharge plasma jet. *Nanotechnologies in Russia*. 2014. № 9. P. 682-687.
20. S.-K. Sun, G.-J. Zhang, W.-W. Wu, J.-X. Liu, J. Zou, T. Suzuki, Y. Sakka. Reactive spark plasma sintering of binderless WC ceramics at 1500 °C. *International Journal of Refractory Metals and Hard Materials*. 2014. № 43. P. 42-45.
- A. Gubernat, P. Rutkowski, G. Grabowski, D. Zientara. Hot pressing of tungsten carbide with and without sintering additives. *International Journal of Refractory Metals and Hard Materials*. 2014. № 43. P.193-199.
21. K.-M. Tsai, Ch.-Y. Hsieh, H.-H. Lu. Sintering of binderless tungsten carbide. *Ceramics International*. 2010. № 36. P. 689-692.
22. L. Cheng, Zh. Xie, G. Liu. Spark plasma sintering of TiC ceramic with tungsten carbide as a sintering additive. *Journal of the European Ceramic Society*. 2013. № 33. P. 2971-2977.