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Planetary mills of periodic and continuous action

E. L. FOKINA, N. I. BUDIM
Institute of Chemistry, St. Petersburg State University, Universitetski pr. 26, Petrodvorets, 198504 St. Petersburg, Russia
V. G. KOCHNEV
Technics and Technology of Disintegration Co., Gdan'skaya 18/1, 194017 St. Petersburg, Russia
G. G. CHERNIK*
Institute of Chemistry, St. Petersburg State University, Universitetski pr. 26, Petrodvorets, 198504 St. Petersburg, Russia
E-mail: chernik@nonel.pu.ru; chernik@GC4548.spb.edu

Laboratory planetary mills have been widely used by researchers studying effects of mechanochemical activation. These mills are usually of the batch type (they need periodic loading-unloading). Scaling up of the planetary mills was considered to be intrinsically impossible. In the recent years successful technical solutions for the problem of continuous feeding of a material into the jars (drums) moving at very high speeds was found, and viable machines operating in the continuous mode have been made. Industrial planetary mills of productivity ranging from 20–70 kg/h to 3–5 t/h (for the powders of -10 μm fraction) have been manufactured and used in mining industry (for gold and diamond recovery from ores). The paper discusses the possibilities of the novel grinding equipment. Investigation of milling of cemented tungsten carbide (WC/Co) and of the WC/Co tools inserts coated with TiN showed that grinding of these hard materials to micron and submicron scale of particles can be performed in several minutes. High efficiency of grinding was demonstrated for a number of materials (graphite, Mo concentrate, MgO).

1. Introduction

1.1. Planetary mills of periodic and continuous action

A great number of processes in industry involve grinding of various materials and treatment of powders. These processes are traditionally performed in ball mills which tend to be large and slow. The idea of using centrifugal acceleration field instead of gravitational field resulted in the advent of novel grinding equipment of the planetary type. During the recent decades of the development of mechanochemistry considerable attention was given to the planetary-centrifugal mills [1–6].

Planetary mills normally have three or four drums rotating around a common central axis and simultaneously around their own axes. The principle of the planetary mill operation has been known for more than hundred years. Laboratory planetary ball mills of the batch type have been used for various purposes including mechanical alloying experiments [1–7]. However, it was noted that manufacturing of planetary mills of high throughput rate encounters design difficulties [6]. An opinion exists that scaling up for larger volumes of powder production in a planetary ball mill is intrinsically impossible [8].

In order to attain high productivity of the planetary mill, continuous feeding of a material into the jars moving at very high speeds and continuous unloading of the product should be provided. During the past decades the problem of continuous feeding of a material into a planetary mill has been successfully solved, and novel planetary mills of the industrial scale operating in *a continuous mode* are now manufactured [9–11]. In this mode the initial material is continuously fed into the mill, with coarse powder returned for another cycle of grinding and the final fine or nanoscale powder product continuously provided as a result of the milling process. The productivity per unit volume of the working chamber for these mills is significantly (at least ten times) higher than that for conventional ball mills. Industrial planetary mills of continuous action, characterized by accelerations of 20 g and by productivity up to 3–5 tons of powder (of minus 10 microns fraction) per hour, are now commercially available [11]. Industrial planetary mills have been used in mining industry (for gold and diamond recovery from ores). Manufacturing

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*Author to whom all correspondence should be addressed.

of a laboratory planetary mill specially designed for the use in research in the field of mechanochemistry (with accelerations 50–100 g) is planned. The energy density in these mills is 100–1000 times higher than the energy density used earlier in conventional milling equipment. It is known that powders undergoing high-energy ball milling are mechanically activated and possess a number of new useful properties: higher reactivity, lower sintering temperature, higher density and improved mechanical and electrical properties [12, 13]. Due to the smaller size of the chamber and short periods of milling, planetary mills provide better purity of the powder product than conventional milling equipment.

The aim of the paper is to test possibilities of the planetary mills. Several applications of the planetary mills will be described. Results of grinding of cemented tungsten carbide will be presented as an example of grinding of a very hard material.

1.2. Recycling of hard alloys

Hard alloys are based on tungsten carbide (WC) or carbides of other metals; most carbides use cobalt as a binder. Research in the field of fine and nanoscale WC/Co powders is actively developing. The traditional method of making WC/Co cemented carbides is by crushing, grinding, blending and consolidation of the constituent powders. The microstructural scale of the WC/Co cemented carbides, which can be no smaller than the size of the milled powders, is typically 1–10 microns in diameter. It is only with great effort that the microstructural scale can be reduced to about 0.5 micron in premium WC/Co grades prepared by the traditional method [14]. New techniques of synthesizing nano-grained WC/Co composites are being developed which do not involve milling of WC/Co; however, these approaches are not applicable to the problems of recycling of hard alloys.

Only a minor part of hard alloys produced in the world is recycled. Recycling hard alloys scrap and waste of their industrial production could halve the need in tungsten for instrumentation purposes. The costs of WC production from primary tungsten metal are 4 times higher than those of tungsten carbide recycled from scrap. Coarse recycled WC/Co powders can be used for applying wear-resistant coatings and for wear-resistant composites. Finely dispersed powders are applied for hard alloy ware manufacturing (a certain share of the recycled powder can be added to the furnace charge without changing standard technological parameters), for electro-erosion materials and for dispersion-strengthened alloys.

There exist two main approaches to recycling WC/Co scrap: chemical and mechanical recycling. The chemical approach is multi-stage and laborious; it requires high energy spending and special metallurgical and chemical equipment. The second approach is mechanical recycling. The processed scrap undergoes crushing, wet grinding and sieving. Mechanical destruction of hard alloy ware is a laborious task. At present it is performed with the help of conventional ball mills.

To characterise the difference in productivity of the planetary mills it is sufficient to say that a cycle of dispersing hard alloy WC/Co from 3 mm particles scrap to 3 micron particles is 70–80 h in a conventional ball mill and 3 min in the modern planetary mill.

In cutting tool industry coated tools are widely used nowadays. Coatings are diffusion barriers, and they prevent interaction between the chip formed during machining and the cutting material. Typical coatings are titanium nitride (TiN), titanium carbide (TiC) and alumina (Al_2O_3) which are extremely hard, thus very abrasion resistant. All these compounds enable inserts to cut at much higher speeds than is possible with uncoated cemented carbides. It is estimated that 80% of carbide tools today are coated [14]. The presence of a hard coating makes the task of recycling of tools inserts even more difficult. In the present work grinding of coated and uncoated WC/Co hard alloy scrap has been studied.

2. Experimental

One sample of the ground material was WC/Co hard alloy scrap (VK-6, Russia), containing WC and 6% cobalt. Another sample was prepared by crushing of rejected tool inserts from the UK. The tool inserts were made of WC/Co hard alloy and coated with titanium nitride (TiN) coating. A planetary-centrifugal mill of the batch type, MPL-1, and that of industrial type, MP-0 (Technics and Technology of Disintegration (TTD), St. Petersburg, Russia) were employed. Granulometry analysis was performed using a laser diffraction granulometer FPS ANALYSETTE 22. X-ray diffraction analysis was performed by means of a DRON 4 M (Burevestnik, St. Petersburg, Russia) X-ray diffractometer. Emission spectroscopy (DFS-13, Russia) was used to determine the contents of iron.

3. Results

3.1. Grinding of the WC/Co sample (VK-6)

The hard alloy WC/Co scrap sample was first crushed in an industrial crushing device to a particle size of 1 and 1.6 millimetres. After that the particles were ground in the industrial planetary mill of continuous action MP-0. The data on kinetics of grinding are presented in Table I. The productivity of the mill can be estimated from Table II.

In the planetary mill of continuous action the particles pass through a classifier, and those particles which are larger than a certain size are returned into the grinding chamber. The data indicate that grinding of hard alloy WC/Co particles of the sizes smaller than 1 and 1.6 mm was highly efficient. The process is justified

TABLE I Average particle size dependence for the WC/Co (VK-6) sample upon time of grinding in MP-0 mill

Time of grinding (min)	Average particle size, d_{50} (μm)
0.5	2.75
1	1.24
2	0.78
4	0.75
8	0.99

TABLE II Share (wt%) of the powder of the WC/Co (VK-6) sample which passed the 40 microns sieve, as a function of time of grinding

Time of grinding, min	Yield of (-40 μm) powder (%) Max feed dimension 1 mm	Yield of (-40 μm) powder (%) Max feed dimension 1.6 mm
0.5	18.2	12.7
2	69.1	45.2

even if only 15% of the material is ground to the required size during a single cycle. The yields of the (-40 μm) powder fraction after grinding for 2 min are significantly higher (69.1 and 45.2% for the feed particles smaller than 1 and 1.6 mm, respectively).

The granulometry data for the WC/Co sample with particles smaller than 1 mm after grinding for 8 min (powder fraction (-40 μm)) are given in Fig. 1 ($d_{50} = 1.6$ μm, $d_{90} = 7.8$ μm).

In Fig. 1 a significant maximum is observed for the average size of 300 nm and smaller maxima at about 1.5, 4 and 9.5 μm.

The contents of iron in the sample obtained from the emission spectroscopy measurements equals 0.06 wt%, i.e., is lower than the required 0.1 wt%.

3.2. Grinding of the WC/Co sample with a TiN coating (from the UK)

The rejected tools inserts had a thick TiN yellow coating; the thickness of the coating was estimated from the X-ray diffraction experiment to be larger than 3 μm. The inserts were crushed to grains of 3–4 mm and then ground in the planetary centrifugal mill (smallest laboratory type mill MPL-1, acceleration 28 g) for 15 min. After that a size fraction of the powder smaller than 44 microns was taken. About 95% of the material obtained after grinding passed the 44 microns sieve.

The results of the particle size analysis for the powder fraction (-44 μm) of the WC/Co sample with a TiN coating after grinding (from particles smaller than 4 mm) for 15 min are given in Table III.

TABLE III Granulometry results for the powder fraction (-44 μm) of the WC/Co sample with a TiN coating after grinding for 15 min ($d_{50} = 3.09$ μm, $d_{90} = 12.16$ μm)

Fixed percentage volumes (%)	Undersize (μm)
30.00	<2.60
40.00	<2.80
50.00	<3.09
70.00	<4.34
90.00	<12.16

TABLE IV The dimensions of the regions of coherent scattering in various crystallographic directions (hkl) for the (-40 μm) powder fraction of the WC/Co sample with a TiN coating

hkl	Regions of coherent scattering (nm)
001	65.0
100	44.0
101	40.0

The results indicating this small size of the particles are supported by the X-ray diffraction data for the WC/Co sample with a TiN coating shown in Figs 2 and 3. We observe significant broadening of the diffraction peaks for the powder obtained for this sample after processing in the planetary mill. On the basis of these data the values of the regions of coherent scattering and microdeformations were calculated. The dimensions of the regions of coherent scattering in various crystallographic directions are presented in Table IV. It can be seen that the dimensions of the regions of coherent scattering are of the tens of nanometers scale, i.e., significantly smaller than 1 micron. The magnitude of microdeformations has been calculated to be only 0.1%. Thus, the main contribution into the broadening of the diffraction maxima is caused by the dispersity of the powder and not by the microdeformations. A conclusion can be also made that the particle size diminishes uniformly in all the crystallographic directions.

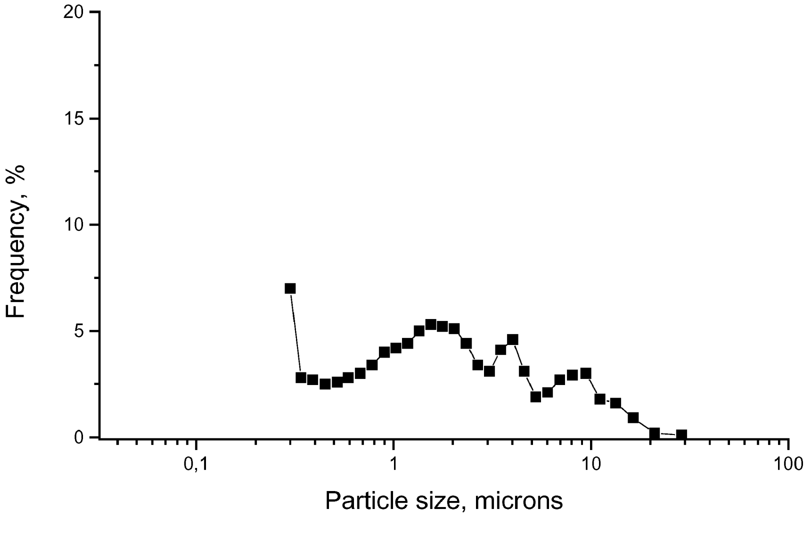

Figure 1 Frequency distribution for the (-40 μm) fraction of the WC/Co (VK-6) sample after 8 min of grinding in the planetary mill MP-0 from the (-1 mm) fraction.

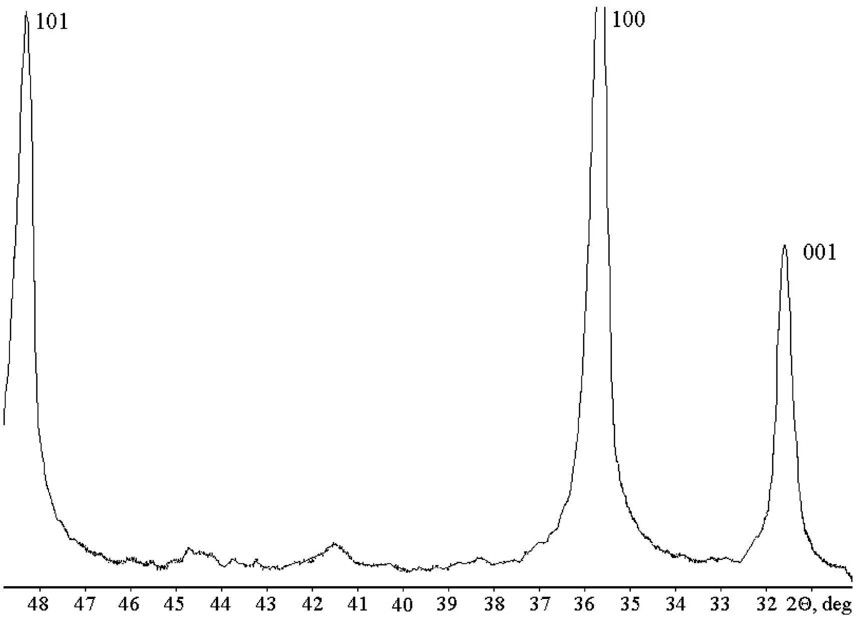

Figure 2 X-ray diffraction pattern of a WC/Co sample with a TiN coating after crushing tool inserts to particles of 4 mm.

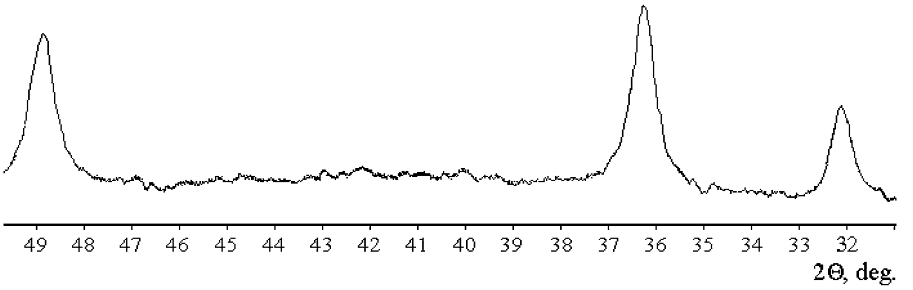

Figure 3 X-ray diffraction pattern of the (−44 μm) powder fraction of the WC/Co sample with a TiN coating after processing for 15 min in a planetary mill MPL-1.

4. Discussion

One can see that in this work the micron-scale size of WC/Co particles is attained in the first *minutes* of grinding, whereas many hours are needed to perform a cycle of comminution of WC/Co scrap in the conventional ball mills. A substantial share of the product powder has particles size smaller than 300 nm, which indicates that the present approach is promising for producing ultrafine WC/Co powder. This is an important result as it is known that the fracture toughness and strength are increased when the average particle size of the hard carbides is reduced [14].

The required purity levels (for iron content) were attained in recycling of the WC/Co (VK-6) sample in this work.

It has been shown above that the task of recycling tool inserts having a hard coating like TiN can be successfully solved by grinding in planetary mills. Optimal regimes of grinding hard alloy scrap to the required size of the particles can be found and adaptation of the technology to specific applications can be performed.

The minimum productivity in grinding of WC/Co hard alloy can be estimated as 20 kg/h for the smallest industrial planetary mill MP-0. One can make a conclusion that recycling of hard alloys can be performed with a substantially higher productivity and lower costs using novel superhigh-energy planetary milling equipment.

Recycling by means of grinding to fine and superfine powders of various solid materials such as glass, refractories, construction materials, etc., is possible. Grinding of hard materials such as oxides, carbides and nitrides, can be performed with high efficiency. Silicon carbide, quartz, alumina and zirconia can be ground to microns sizes in several minutes [11].

Efficiency of grinding can be estimated by comparing time of milling for the TTD smallest size laboratory MPL-1 mill and for a well-known laboratory planetary mill available in the market which serves here as a reference mill (accelerations in it normally do not exceed 12 g). The materials studied were graphite, molibdenium (Mo) ore concentrate and magnesium oxide (MgO, periclase). From Table V one can see that a comparable average particle size of the powders is obtained in the TTD mill at least 10 times faster than in the reference mill. For the MgO sample comparable submicron size of the particles is obtained in 4 min in the TTD mill, whereas 6 h and a half of milling are needed when grinding is performed in a reference mill. These results are explained by the significantly higher acceleration and energy density of the TTD mill.

TABLE V Comparison of the results of grinding of materials in the TTD MPL-1 mill and in the reference mill

	TTD mill		Reference mill	
Material	d_{50} (μm)	Milling time (min)	d_{50} (μm)	Milling time (min)
Graphite	30.5	30	46.7	290
Mo concentrate	0.53	30	0.80	290
MgO	0.55	4	0.42	390

5. Conclusions

Laboratory planetary mills of the batch type have been known and applied in various fields. Technical solution of the problem of continuous feeding of the material into the planetary mill resulted in the creation of the industrial scale planetary mills operating *in the continuous mode*. Novel planetary mills employ substantially higher accelerations and energy densities than conventional milling equipment. Investigation of milling of cemented tungsten carbide (WC/Co) and of the WC/Co tools inserts coated with TiN showed that grinding of these hard materials to micron and submicron scale of particles can be performed in several minutes. High efficiency of grinding was demonstrated for a number of materials (graphite, Mo concentrate, MgO). Fields of possible applications of these novel planetary mills include recycling of hard alloys, powder metallurgy, recycling of solid waste, ceramic and chemical industries and manufacturing of construction materials.

References

1. V. YU. MOLCHANOV and T. S. YUSUPOV, "Physical and Chemical Properties of Finely Dispersed Minerals" (Nedra, Moscow, 1981) (in Russian).
2. V. V. BOLDYREV, "Experimental Methods in Mechanochemistry of Inorganic Substances" (Nauka, Novosibirsk, 1983) (in Russian).
3. G. HEINECKE, "Tribochemistry" (Akademie-Verlag, Berlin, 1984).
4. E. G. AVVAKUMOV, "Mechanical Methods of Activation of Chemical Processes" (Nauka, Novosibirsk, 1986) (in Russian).
5. A. Z. JUHASZ and L. OPOCZKY, "Mechanical Activation of Minerals by Grinding: Pulverizing and Morphology of Particles" (Akademia Kiado, Budapest, 1990).
6. V. V. BOLDYREV, "Mechanochemical Synthesis in Inorganic Chemistry" (Novosibirsk, Nauka, 1991) p. 5.
7. F. SCHURACK, I. BORNER, J. ECKERT and L. SCHULTZ, *J. Metastable Nanocryst. Mater.* **2–6** (1999) 49.
8. H. ZOZ, D. ERNST, I. S. AHN and W. H. KWON, in "Synthesis/Processing of Lightweight Metallic Materials," edited by C. M. Ward-Close, F. H. Froes, S. S. Cho and D. J. Chellman (TMS Annual Meeting, 1997).
9. V. G. KOCHNEV and S. A. SIMANKIN, Planetary Mill Feeder, RU Patent 2094120 (1994).
10. V. G. KOCHNEV, Planetary Mill, RU Patent 1358990 (1992).
11. http://www.ttd.spb.ru
12. V. V. BOLDYREV, V. I. LAPSHIN, E. L. FOKINA and V. K. YARMARKIN, *Dokl. AN SSSR, Tekhn. Fiz.* **305** (1989) 852 (in Russian).
13. N. I. BUDIM, V. I. LAPSHIN, G. D. RUBALSKI and Y. N. KRASIK, *Poroshkovaya Metallurgiya* **11** (1991) 96 (in Russian).
14. ZH. YAO, J. J. STIGLICH and T. S. SUDARSHAN, http://www.matmod.com and references therein.

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