**Process Development: Low Cost, Continuous
Nano-Scale Purification Technology of Powered
Carbonaceous Materials for Applications in
Electrochemical Energy Storage Systems and
ELECTROCONSOLIDATION® Process Technology**

Nuclear Engineering Division

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prepared by
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September 30, 2010

Final Report on Superior Graphite CRADA C0300901
Argonne National Laboratory
Technical Monitors: N. Gopalsami and A. C. Raptis
Lab POC: D. Ehst

Title: Process Development: Low Cost, Continuous Nano-Scale Purification Technology of Powdered Carbonaceous Materials for Applications in Electrochemical Energy Storage Systems and ELECTROCONSOLIDATION[®] Process Technology

CRADA Partner: Superior Graphite Co., Chicago, IL

STCU partners:

- (1) IPOCC working on thermochemical purification,
- (2) KNUTD working on chemical graphite purification,
- (3) KIPT working on Electroconsolidation of ceramic near netshape parts, and
- (4) Feroservice working on pilot plant installation of mature technologies

Period of Performance: January 2005-December 2009 under P514 and December 2009-March 2010 under P154a Extension

Total cost of the project (including in-kind): \$3,407,600.00

Objectives: (a) to develop carbon purification technologies for electrochemical energy storage application and (b) to build the next generation Electroconsolidation system to produce special purpose parts for niche markets.

Summary: The project has met all major milestones. The status and accomplishments of each institute are highlighted below.

1. KIPT—The Electroconsolidation process technology is built and running in a manner beyond what we envisioned. Novel products include those for dental implants, and neutron absorber rods. The road to commercialize these products will take time, but they are unique, and could lead to some business for the institute in either a licensing arrangement with outside parties, or with small scale production on-site.
2. KNUTD—A batch-processing chemical purification method was developed, and they reached a purification goal of 95% C early on. This group then moved on to purify product to 99% or higher level via commercial and novel methods. Superior Graphite is trying to create a joint venture together with a local partner/supplier of raw material to utilize some of the intellectual property created during the project.
3. IPOCC—The thermo-chemical purification method ran into a technical hurdle of having higher than allowable trace quantity of molybdenum in their purified product, but they developed a method to separate kish graphite mechanically

based on which a pilot plant was installed by Ferroservice. The goal of the nano-scale method to purify carbon-based product was reached only as the program ended. More work will have to be done to further develop this concept for its eventual commercialization.

4. Ferroservice—Installed a pilot plant based on IPOCC's method to separate kish graphite mechanically. This method was then further developed/refined into a semi-commercial method of separation. Whether this process can be fully utilized in a commercial way is still under consideration.

See attached technical report for details of the developed technologies.

**Final Report for GIPP Projects P-154 and P-154a on
Process Development: Low Cost, Continuous Nano-Scale Purification
Technology of Powdered Carbonaceous Materials for Application in
Electrochemical Energy Storage Systems and Electoroconsolidation® Process
Technology**

By

**Edward O. Carney, President and CEO, Superior Graphite
and**

Sami Gopalsami, Technical Monitor, Argonne National laboratory

31 August 2010

Initial scope

Argonne in partnership with Superior Graphite and three Ukrainian institutes, applied for, and its application was accepted for funding under the Global Initiative for Proliferation Prevention program of DOE/NNSA. Its purpose was (a) to develop carbon purification technologies for electrochemical energy storage application and (b) to build the next generation Electroconsolidation system, invented by Superior Graphite, to produce special purpose parts for niche markets. Our program started in 2005 under the STCU project number P-154. In September, 2009, a 6-month extension to complete some of the outstanding work was granted, and these activities were designated under P-154a. This work concluded at the end of March in 2010, and final visits were made in June, 2010 to recognize and acknowledge the accomplishments of the group.

Superior Graphite partnered with 3 institutes in Ukraine; IPOCC (Institute for Physical and Organic Coal Chemistry in Donetsk), KIPT (Kharkov Institute of Physics and Technology in Kharkov) and KNUTD (Kyiv National University of Technologies and Design in Kyiv). In addition, there was participation from Private Company Ferroservice in Donetsk. Initially, Superior Graphite was joined by Columbian Chemical Company as a joint partner, however, along the way their focus changed and they chose to back away from the program. Argonne National Laboratory was the project leader throughout.

The initial program foresaw 2 possible outcomes; 1) the establishment of Superior Graphite's Electroconsolidation process technology with KIPT in Kharkov, and 2) the development of nano-scaled technologies to purify carbon-based materials for application in the electrochemical energy storage systems with IPOCC, with intermediate upgrading of the carbon-based product by KNUTD. By the end of the program, 2 additional bodies of work were created; 1)

one was an off-shoot of the project being done at IPOCC where kish processing and upgrading was added to the overall program, and 2) because of the delay in some of the work being done at IPOCC on the nano-scaled purification, KNUTD created a method to chemically purify carbon-based materials.

Involvement of STCU

Throughout the program, we were fortunate to have the Science and Technology Center (STCU) in Ukraine manage the program on a local basis. They would take the reports submitted by the institutes, ensure the deliverables were being met and spending under control, translate the reports, and recommend approval of the expenditures on a quarterly basis. From the beginning, there has been a lot of continuity in terms of who was managing the program.

Challenges encountered along the way

It is not surprising that given the length of the program (5 years), that there would be a number of challenges. Of course, there were technical challenges we encountered, but also certain philosophical ones along the way. Early on, we changed the scope of the Electroconsolidation work to include a market study to ensure there was enough of a market need to locate the Electroconsolidation process there. Later, there were problems with payments - both out-going and incoming. On occasion, we protested the expenditures being made on some of the projects, and withheld payment to our partners when either the work was not getting done, or progress reports were not done in a timely fashion. On the incoming side, there was a period of about 9 months when no money flowed to the projects (because of DOE order), and work on the projects basically stopped. In the beginning, the reports and time sheets arrived within an acceptable period of time, and towards the end, it could sometimes be cumbersome to get the reports done. After about a year of the original project, Columbian Chemical pulled back on its interest in the project. Superior Graphite had some challenges in personnel managing the project when the most senior person knowledgeable on the Electroconsolidation process left for another opportunity. In addition, the person overseeing the management of the program, Dr. Igor Barsukov, was let go from Superior Graphite in the downturn of 2009. From Argonne's side, there were a number of project managers/technical managers starting with Iouri Prokofiev, then moving to Paul Raptis, and finally to Sami Gopalsami. Despite the number of challenges along the way, the spirit of cooperation remained.

Project deliverables

Relative to the original deliverables, there was some good success to report on, but one project (IPPOC) took a little longer to achieve the deliverable, which only came in the last weeks of the program's existence. We will say that the project (KIPT) that started out furthest back (in the race towards success) due to the addition of the market study, was the one that seemed to have the greatest success. Some of this, we acknowledge, was due to the fact that the technology existed before, and therefore the technical leap needed was maybe not as great, however, we will give the team at KIPT great credit for achieving success the fastest of the groups, and for coming up with some very novel ways to utilize the technology. On the other side, IPOCC took a lot of time to create the technology they had envisioned. Basically, it was not until the last month of P-154a that they were able to achieve purification levels they were seeking.

Due to the latter delay at IPOCC, 2 projects were added as is referenced above. The kish processing and upgrading was a unique side project started in the lab that eventually made it to a pilot scale at the private company, Ferroservice (it was originally intended that Ferroservice would house the nano-scale purification). Ferroservice made a valiant effort to take the lab scale process to pilot scale, and though they did not meet the throughput goal that was projected when going from lab to pilot scale, it was not due to lack of effort.

The second project that was added on the chemical purification of carbon-based materials was also due to the delay at IPOCC. It was the original intent for KNUTD to evaluate and source local material and to recommend a means to upgrade from roughly 89% carbon content to 95%. This intermediate material would then be furnished to IPOCC for final purification. After roughly 3 years of essentially waiting for the IPOCC, KNUTD took it upon themselves to further upgrade carbon-based material to 99,9% and above. Though some of this technology is commercially available, there is some novelty in what they have proposed, though there are also significant environmental concerns.

In summary, many of the intended deliverables were met. At times, it was not clear whether they would be, and at times there were departures from the intended course. There were, however, successes from which our company can build, and are trying to do so with the continued involvement of the institutes where it makes sense.

Overall Assessment

According to the goals that were identified by STCU for the GIPP program, “engaging FSU scientists and teaching them western business practices, thereby increasing their potential for long-term income and outside employment outside the proliferation area,” we do believe our involvement together with the institutes we have worked together with has resulted in success. While that success might not be as tangible for any of the parties as it stands right now, we do believe this will be achieved over time.

As for specific achievements of the projects, those are listed below:

- 1) **KIPT** – The Electroconsolidation process technology is running in manner beyond what we envisioned. Novel products include those for dental implants, and neutron absorber rods. The road to commercialize these products will take time, but they are unique, and could lead to some business for the institute in either a licensing arrangement with outside parties, or with small scale production on-site.
- 2) **KNUTD** – Purification goal of 95% C was reached early on. This group then moved on to purify product to 99% C and above via commercial and novel methods. Superior Graphite is trying to create a joint venture together with a local partner/supplier of raw material to utilize some of the intellectual property created during the project.
- 3) **IPOCC** – The nano-scaled method to purify carbon-based product was reached only as the program ended. Thus, not much was able to be done at such a late stage. More work will have to be done to further develop this concept for its eventual commercialization.
- 4) **Ferroservice** – The method to separate the kish mechanically was developed by IPOCC and installed at Ferroservice. This method was then further developed/refined into a semi-commercial method of separation with the good work done by Ferroservice. Whether this process can be fully utilized in a commercial way is still under consideration.

We can also say that we have enjoyed the relationships we have built with the people involved in our projects, and have been able to bridge any cultural gaps fairly easily. While it has not always been easy to follow the developments in each of the projects, due to the time difference and distance some of that

improved over time as we began to see some of the achievements. The scientists we have worked with, while not having all the modern tools, were competent, and were well-equipped enough to seek input from outside their realm of expertise.

None of this would have been possible, were it not for the U.S. State Department's understanding of the importance of building bridges in sometimes remote places. Their funding of this program helped ensure that all parties felt as though something important was achieved. We also applaud the efforts of STCU and ANL, who were the administrators of the program from both sides. Their insights and oversight has been invaluable. I (EC) can say, there is no way our company could have undertaken something like this on our own.

While we hope to be able to establish some meaningful business and ventures in the future, time will tell. It is clear that in some cases, it will be difficult for us to do so – in other words, the challenges may still be too great. We do, however, have a couple of means to further our work there to see if we can eventually work toward pilot or full-scale production.

Respectfully submitted,

Ed

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Process Development: Low Cost, Continuous Nano-Scale Purification Technology of Powdered Carbonaceous Materials for Applications in Electrochemical Energy Storage Systems and ELECTROCONSOLIDATION® Process Technology

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Financing parties: USA

Operative commencement date: 01.01.2005

Project duration: 4 years

Project technical area: development of new materials and advanced technologies

Reported stage: 15

Date of submission: 26.06.2009

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Summary

IPOCC & Ferroservice:

During report quarter, we made fitting to site, mounting, and perfection of separate elements of basic technological equipment of the pilot unit for upgrading of kish graphite. Actually, technological and electrical manifold of equipment has been completed. Technological testing was carried out successfully with separate elements of equipment such as magnetic separators, mills, air separating columns, auger and vibrating feeders. Arising difficulties were obviated in close cooperation between IPOCC and Ferroservice teams. Considering the results of material balance, calculation of prime cost of upgraded kish-graphite has been made for pilot unit and scaled industrial technology. It was shown that industrial unit for kish upgrading with capacity of 1200 ton per year provides the production of competitive product with prime cost about \$430 per ton working at renewable source of raw. In our opinion, this will provide high competitiveness of planned production.

KNUTD team has completed the making and testing of the laboratory demo line for single-stage purification of kish graphite (that is acidic treatment) including conceptual workup of the question of neutralization and sewage treatment.

At this processing line, we have made the samples of purified kish-graphite; the samples were studied and sent to USA for testing.

The results of testing show that taking upgraded up to 95% kish graphite as initial material and using the single-stage of acidic treatment, one could be successful obtaining ~ 99.3-99.5% C graphite, which virtually fits the requirements

of battery trade (excluding some excess of aluminum and chrome impurities). Using of full cycle of chemical treatment for kish graphite enables one to obtain high-pure graphite with carbon content no less than 99.9%.

The problem of application of industrial equipment for commercialization of this process has been worked out.

The draft of patent disclosure for chemical purification of graphite has been drawn up.

During forthcoming visit of US Partners to Ukraine, it is necessary to decide, when and in which form this application will be applied to patent authorities of Ukraine and USA, and also, to prepare a business document, which will guide future commercial relationship between SG and KNUTD.

The quarter under review (ECT-12) has resulted in the following: imperfections in the pilot EC[®] facility performance have been analyzed; ways of improving the EC[®] facility have been drawn up; lines of development of absorbing materials for commercial nuclear power reactors have been devised; relationships have been established between the density and structure formation peculiarities of dysprosium titanate/hafnate pellets and the hot pressing temperature; one of the most radiation-resistant structures, namely, the fluorite structure has been produced by the EC[®] technology in dysprosium hafnate pellets; absorbing pellets from dysprosium titanate and dysprosium hafnate have been produced for further studies and evaluation tests; special features of nanometric powder product forming and sintering.

Introduction

IPOCC & Ferroservice: At the phase, the teams have focused their efforts on mounting and running-up the pilot unit that realizes recently developed technology of upgrading of kish graphite starting from 25% content of carbon and produces 95% end product. The second task was to estimate the economical effectiveness of the pilot unit and the industrial process at scaling of the unit up to production rate of 1200 ton per year.

In connection with the fact that work on kish graphite was planned as the nearest purpose for commercialization of designings, KNUTD team task consisted in approbation of recently developed laboratory technology for chemical purification of kish graphite.

The main content reflects the obtained results both in the area of chemical purification of kish graphite and in the area of selection of the equipment, which is necessary for building of the operating pilot unit.

From among the production processes involving the use of the EC[®] technology, which were developed in the framework of Project P-154 in years 2007-2008, of most acceptance have appeared by the present time in Ukraine the processes that provide the production of the following products:

- pellets from promising absorbing materials based on dysprosium titanate/hafnate for final control elements of nuclear reactor control and protection systems;
- nozzles from Al₂O₃(95%)- and boron carbide-based ceramics for sand blasters and argon-arc welding;
- ball-and-seat seals;
- hard alloy matrices for manufacture of superhard materials;
- indexable inserts;
- milling body;
- ceramic components for dental ZrO₂-base implants.

At this stage, the main attention was given to the development of absorbing materials and to mastering of nanoceramic product manufacture procedures.

Technical approach

IPOCC & Ferroservice: One of the tasks of the phase was to study the workability of designed non-standard equipment made before in the conditions of operation of industrial pilot unit for upgrading of kish graphite. For the purpose, job family has been carried out that included adjustment and testing of magnetic separators, mills, air separating columns, auger and vibrating feeders. Since, unlike to laboratory unit, which operates pressurized column of air separation, columns of air separation in pilot unit are parallel connected and work at underpressure, this required the possibility of independent control of the flow in every isolated column. Also, sector unloaders of original design were mounted to provide sure unloading of graphite from depressed zone.

Setting the pilot EC[®] facility into operation has permitted the realization of a number of technological processes developed specially for the facility when producing pilot blank parts and runs of items.

Experiments have demonstrated that the EC[®] facility can provide at this time the production of small pilot batches of the following items: dysprosium titanate/hafnate pellets, milling bodies, nanometric powder articles.

I-1.1 Installation of the process equipment and monitoring instruments for the plant of kish graphite beneficiation

Recently, we have designed and made the complete of non-standard equipment for the technology of dry upgrading of kish graphite. Also, standard equipment such as cribs, fans, reduction gears, hot-wire anemometers, and

other was purchased. At the territory of Ferroservice Co., production floor space has been chosen; layout diagram referred to chosen housing was developed. (see Reports T13-T14).

At the present phase, mounting of capital equipment has been done, and technological and electrical manifold is virtually completed. During installation, technological testing of separate units of equipment was carried out. Appearing problems were solved in the course of work.

Pilot unit is located in the room, which is larger a little than standard 20-feet shipping container. The unit is made in the form of two main modules: the module of primary magnetic separation of initial kish graphite and the module of final purification of intermediate product.

In so doing, outer dimensions of the first module are of about 25% of the whole unit, i.e., it may be performed in untethered (mobile) version to be installed at the plant-supplier of kish graphite.

Physical configuration of the unit during mounting and manifolding operations is presented on Fig I-1.1.1a and Fig I-1.1.1b.

a) – lower story of the unit

b) – upper story of the unit

Fig I-1.1.1 The appearance of the unit of dry upgrading of kish graphite during mounting and manifolding operations

Among the problems, which we had to solve while mounting and testing of separate elements of the unit, one of the main ones became the problem of **vertical feeding of initial kish graphite** from loading hopper up to the level of about three meters. It turned out that specified screw auger with length of 700 mm does not provide feed motion of material to the required level. In order to solve the problem, it has been proposed to elongate the screw auger by way of its advance by spiral auger wound of thick steel wire. The solution being successful allowed us to achieve efficiency of 15 kg per hour already at the first examination. In order to provide required efficiency of 120 kg per hour, more powerful gear-motor drive with higher rotation rate was implemented; the hopper was additionally equipped with vibrator. This has provided increasing of feeding of initial graphite to required level.

By analogous way, all feeding horizontal augers were lengthened. Checking has shown that, at horizontal feeding of high-ash residue after magnetic separation, such augers have throughput at the level no less than 80 kg per hour that is close to design value and provides trouble-proof continuous operation of the unit.

It became clear **at assembling and adjustment of magnetic separators** that the construction with variable magnetic-field strength, which we had designed, turned to be very successful; it provided us for exact setting of required parameters of magnetic field. According to modern tendencies, we implemented the gradient scheme of magnetic field with constant peak value of magnetic field strength in the sector of 180° along material movement and its further decreasing by 2 and than by 4 times at the sector of unloading of magnetic fraction. As analysis of modern tendencies shows, gradient pattern of magnetic field allows to increase upgrading rate of material due to multiple passing of reversal zones of magnetic field strength.

The profile of magnetic field around the drum circle of separator is shown on Fig I-1.1.2a, and the profile of magnetic field along the drum generatrix – on Fig I-1.1.2b.

a. – around the drum circle (measured at the middle of drum width, 0 degrees at the top of drum)

b. – along the drum generatrix (measured at the line of maximal amplitude)

Fig I-1.1.2 The profile of magnetic field strength of magnetic separator

The results of testing of adjusted magnetic separator on real initial kish graphite have shown that, at load of 96 kg per hour, it has been obtained 28.3% of submagnetic fraction with ash content of 35.2% and 71.7% of strong-magnetic fraction with ash content of 88.7%. At the same time, the level of carbon extraction for the only run was of 69.3% that is just some better than it was achieved in laboratory conditions.

For the purpose of reducing of the costs for equipment, **simple and failsafe vibrating trays** have been made for uniform supply of kish graphite to magnetic separators (Fig I-1.1.3).

Fig I-1.1.3 Vibrating trays for supply of kish graphite to magnetic separator (during mounting)

At trial run of **mills of soft grinding of kish graphite** (Fig I-1.1.4), it has been found that hard vibrations and noise are observed at high rotations. The problem was eliminated by way of static balancing of rotors.

Fig I-1.1.4 Centrifugal (ventilator) mill for soft grinding of kish graphite

At subsequent trials, it has been found out that spurious air flow as concomitant of mills operation is very strong; this makes impossible any passing of ground material onto vibration tray. Besides, such an air flow makes sonic boom. In order to eliminate this disadvantage, exhaust of mill was fitted with cyclone with rotary unloader, and a diaphragm with controlled gap was installed at the mill inlet and at the cyclone outlet for decreasing of air flow velocity.

One more task was providing with reliable **measurement of air flow velocity** within air-separating columns. Primarily, in the laboratory conditions we used float-type rotameter RM-40GUZ (Fig I-1.1.5a) that provides sure monitoring of air volume velocity. However, concerning the pilot unit being built and in the conditions of the room with restricted height, the decision has been made to use more compact digital hot film thermo-anemometers EE75 (Fig I-1.1.5b, c). The probe of thermo-anemometer mounted in the column is shown on (Fig I-1.1.5d).

a. – float-type rotameter RM-40GUZ

b. – thermo-anemometer EE 75, display module

c. – hot-film anemometer EE75

d. – hot-film anemometer EE75 installed in air separation column

Fig I-1.1.5 The outfit for air flow velocity monitoring

All this allowed us to evade encumbering of the unit not only by 7 rotameters but also by taking away 21 flaps and considerable distribution pipeline structure. Besides, this decreased the total height of the unit by more than one meter.

Nevertheless, such replacement has demanded some additional efforts directed to match-making between measurements of volume flow made by rotameter and linear velocity made by anemometer. First of all, it is connected with the fact that a rotameter measures the integral value of air outgo, and anemometer does the measurement of the velocity in the definite point of the flow. *De facto*, it has been found that the velocity profile within the column has the shape represented in diagram on Fig I-1.1.6a, and recalculation of rotameter readings into ones of anemometer one should do according to nomograph that is represented on Fig I-1.1.6b.

a. – air velocity profile within the column

b. – compliance between rotameter readings and air velocity in the center of column

Fig I-1.1.6 Air velocity profile within the column and nomograph of compliance between rotameter readings and air velocity in the center of column

Since the pilot unit comprises a number of electrical blocks, for their connection, we have to design the electrical network, which allows for both technological traits of processes and necessary interlockings. Designed schematic electrical diagram is represented on Fig I-1.1.7. On Fig I-1.1.8, there is mounted control cabinet shown; it provides convenient control of all aggregates of the pilot unit.

Fig I-1.1.7 Schematic electrical diagram of the pilot unit

Fig I-1.1.8 Control cabinet of the pilot unit

At the present phase, the unit is practically assembled, and the main elements was tested and debugged. Arising problems are solved in the regular course of work in close cooperation between Ferroservice and IPOCC teams. For startup of the pilot unit, it is necessary i) to complete communication manifold of the unit according to technological scheme, ii) to check a conformity of mass traffics, and iii) to optimize the modes of operation of separate elements.

I-1.2 Assess the costs of processing of updated kish-graphite

Source data for composition of material balance on the results of testing of laboratory unit are represented in Table I-1.2.1. At the same time, the preliminary stage is twofold magnetic separation of initial kish graphite with intermediate milling of magnetic fraction (is not shown in Table I-1.2.1). The result of such treatment is isolation of 29.4% of concentrate with 38.9% ash content; this goes to further upgrading. Wastes with ash content of 92.05% made up about 70%.

Table I-1.2.1

Parameters of the three successive cycles of kish graphite concentrate upgrading counting on initial kish graphite

Cycle #	Material come into the cycle of upgrading		End product of the cycle of upgrading			Reflux into the next cycle		Wastes of the cycle of upgrading					
								Magnetic fractions		Sieve fraction - 0.05mm		Amount of wastes	
	Share, %*	A ^d , %	Fraction, mm	Share, %*	A ^d , %	Share, %*	A ^d , %	Share, %*	A ^d , %	Share, %*	A ^d , %	Share, %*	A ^d , %
1	29.38	38.9	-1.0+0.05	6.78	4.45	12.98	21.45	72.97	91.41	4.97	98.46	77.94	91.85
2	12.48	20.9	-1.0+0.063	3.05	5.34	7.88	17.27	0.10	61.03	1.35	88.97	1.45	87.04
3	7.88	17.3	-1.0+0.063	1.57	5.04	6.08	20.42	0.04	53.25	0.15	35.15	0.19	38.77
Total***	-	-	-1.0+0.05	11.40	4.77	6.08	20.42	73.11	91.35	6.47	94.95	79.58	91.64

* – accounting on initial kish graphite (-1.0mm).
 ** – wastes of preliminary magnetic separation are also allowed for.
 *** – losses in laboratory batch process are of 2.39%.

Material balance of the technology of kish graphite upgrading is set in Table I-1.2.2.

Table I-1.2.2

Material balance of kish graphite upgrading counting on initial kish graphite

No.	Description	per 100 kg of initial kish	kg per ton of upgraded kish	No.	Description	per 100 kg of initial kish	kg per ton of upgraded kish
1	Initial kish	100	6684.49	1	Updated kish 95% C	14.96	1000.00
				2	Ash waste (90.1% ash)	82.10	5487.97
				3	Losses	2.94	196.52
	Total	100	6684.49		Total	100.00	6684.49

The losses are calculated by the results of operation of laboratory unit. For the pilot one they will make up bits of percent.

Using the data of material balance, one could estimate prime cost of upgraded kish graphite both for pilot unit and for large-scaled industrial production.

For calculation of prime cost, we considered such its constituents as raw stuff, electric energy, wages of skeleton factory personnel, taxes, and depreciation of main machinery. At once, we did not take into consideration such important constituents of prime cost as transport and waste burial charges because they depends very much on particular circumstances of manufacture arrangement. For example, if given manufacture is located on the territory of metallurgical plant (source of raw material) then both mentioned constituents come to null. In other assumption that we use raw kish from Mariupol plants, transport charges are estimated as \$50 per ton of end product for the whole roundtrip (120x2=240 km).

The output of pilot unit counting on updated kish graphite is 12 kg/hr or, at continuous operation, 8.64 ton per month.

Calculation of raw stuff and materials costs is cited in Table 1.2.3.

Table I-1.2.3

Calculation of prime cost on raw and other materials per 1 ton of product

Description	Measuring unit	Price for measuring unit, \$	Qty per 1 ton of product, kg	Cost per 1 ton of product, \$
Initial kish	kg	0.0197	6684.5	132
Total				132

Calculation of expenditures for electricity

Total capacity of technological equipment of pilot unit is	5.4	kW
At output of	12.0	Kg/hour
Expenditure of electricity per 1 ton of product is	446	kWhr
At electricity price of 0.1 \$/kWhr, its cost per 1 ton of product is	45	\$/ton

For calculation of salary, we assume tree-shift schedule of work, continuous three eight-hour shift production; this demands four crews (Table I-1.2.4).

Table I-1.2.4

Stuff list and salary

Position	Qty	Salary, \$/month	Sum, \$/month
Machine-shop manager	0.3	600	180
Shiftman	2	500	1000
Operator/mechanic	8	400	3200
Total			4380
Salary per 1 ton of production is			507\$/t

Costs for procurement of equipment, making, installation, and setup of technological line is of \$90000. Then, subject to output of pilot unit of 8.64 ton per month and its lifetime of 10 years, depreciation charges per 1 ton of production is 104 \$/ton.

Calculation of prime cost of 1 ton of upgraded kish graphite is set in Table I-1.2.5.

Table I-1.2.5

Calculation of prime cost of 1 ton of upgraded kish graphite with carbon content of 95%

Item	\$ / ton	%
Raw & materials	131.7	13.4
Electric energy	44.6	4.5
Capital charges	104.2	10.6
Salary	506.9	51.7
Tax to retirement fund (36.2%)	184.0	18.7
Tax to traumatism fund (2.03%)	10.0	1.0
Prime Cost	981.4	100.0

As show the data of Table I-1.2.5, prime cost of 1 tone of upgraded kish graphite is of \$980 that approximately corresponds to price of natural graphite GT-1 in Ukraine. Obviously, in this case, the share of salary and charges in prime cost of pilot unit is unreasonably high. This is connected with impossibility of manning level decreasing lower the minimal safe norm at low capacity of the unit.

Thus, the product cannot be competitive on free market because of such cost of pilot production. However, it is ought to be considered that this pilot unit is not planned for industrial production; it is aimed exclusively for approbation and approval of concept and for working-out the technology of upgrading of kish-graphite.

The calculations give an opportunity to estimate the prime cost of upgraded kish in the conditions of its full-scale industrial production. Let's now assess product prime cost for production capacity of 100 ton per month i.e. 1200 ton per year.

It is known that spending for raw stuff and materials as well as electricity per unit of production are virtually invariable at scaling. At the same time, in calculation per one ton of product, charges for salary/wages, taxes, and depreciation of equipment decrease significantly with increasing of capacity of production although personnel number and cost of plant grow.

Cost of industrial unit is estimated by known formula: $C = C_0 \left(\frac{P}{P_0} \right)^{0.66}$, where C_0 – cost of base pilot unit, P and

P_0 – outputs of industrial and base pilot units, respectively. Then, considering lifetime of equipment T , spending for its depreciation per unit of production will be $c = \frac{C}{TP}$ \$ per ton.

Wages at industrial production is estimated by formula: $S = S_0 + S_0 \ln \left(\frac{P}{P_0} \right)$, where S_0 – pay of personnel at base pilot unit, P and P_0 – outputs of industrial and base pilot units, respectively.

Initial data for calculation of prime cost of updated kish in conditions of its full-scale industrial production with capacity of 100 ton per month are cited in Table I-1.2.6 and results of calculation – in Table I-1.2.7.

Table I-1.2.6

Initial data for calculation of prime cost of 1 ton of upgraded kish at output of industrial unit of 100 ton per month

New capacity P	100.00	ton / month
Initial capacity P_0 (calculation base)	8.64	ton / month
Scale factor	11.6	
Initial kish price	0.0197	\$/kg
Lifetime T	10	years
Capital equipment cost C	453047	\$
Salary/wages S	15106	\$/month

Table I-1.2.7

Prime cost of 1 ton of upgraded kish at output of industrial unit of 100 ton per month

Item	Cost per ton, \$	Cost composition, %
Raw & materials	131.7	30.6
Electric energy	44.6	10.4
Capital charges	45.3	10.5
Salary/wages	151.1	35.1
Tax to retirement fund (37% to salary)	55.0	12.8
Tax to traumatism fund (2.03% to salary)	3.0	0.7
Prime cost	430.6	100.0

The data of Table I-1.2.7 show that at given capacity of industrial unit, produced upgraded kish could be already quite competitive in Ukrainian market. The structure of cost shows that the weightiest expense item is spending on salary/wages; and taxes are only about 13.5%. Calculated prime cost of \$430 per ton provides undoubted economical attractiveness of proposed technology.

I-1 Conclusions

1. Mounting of capital equipment has been done, and technological and electrical manifold is virtually completed. Technological testing of separate units of equipment was performed successfully. Appearing problems were solved in close cooperation between IPOCC and Ferroservice teams.
2. Considering the results of material balance, calculation of prime cost of upgraded kish-graphite has been made for pilot unit and industrial technology. It was shown that industrial unit for kish upgrading with capacity of 1200 ton per year provides the production of competitive product with prime cost about \$430 per ton working at renewable source of raw. In our opinion, this provides high competitiveness of planned production in Ukrainian market.

I-3.1. KNUTD laboratory demo line for chemical purification of kish graphite.

Fig I-3.1.1 shows the diagram of laboratory demo line for acidic treatment of kish graphite.

Fig I-3.1.1. The process flowsheet of kish graphite purification by means of acidic treatment

1 – distiller; 2 – storage tank for distilled water; 3 – drying oven; 4 – reactor for acidic treatment; 5 – distilled water heater; 6 – filter; 7 – pH meter; 8 – tank with $\text{Ca}(\text{OH})_2$; 9 – filtrate storage; 10 – precipitator; 11 – mechanical filter; 12 – back osmosis water purifier; 13 – centrifuge; 14 – drying oven; 15 – ion exchanger; 16 – compressor.

The scheme was tested and mounted partly at KNUTD (excluding some units for waste-water treatment, namely, 12 and 15, because of lack of means at carrying out of the P-154 Project.

According to developed technological scheme, actually, the process of purification of 95% kish graphite sent by Donetsk team is realized as follows.

A portion of ready-to-be-treated graphite powder is preheated in drying oven (3) at 300 C. Then, it is placed into reactor (4) and concentrated hydrochloric acid is poured in right there. The suspension is vacuumized at continuous stirring and heating for 40-45 minutes in the reactor (4) fitted with stirrer and heat exchanger.

The product is carefully washed on filter (6). Primary washing is performed by back osmosis treated water from return cycle (up to pH ~5-6) and then by hot (70-80 C) distilled water from distiller (1) through storage tank (2) and heater (5). Filtration is to be done until rinsing water at the outlet of filter (6) has pH of 7 and its conductivity becomes equal to that of initial distillate. These conditions only could ensure that soluble metal chlorides was washed out into filtrate from all of the pores of graphite powder.

Neutralization of filtrate with acid reaction is performed in storage tank (9) by lime milk from tank with $\text{Ca}(\text{OH})_2$ (8). Both vessels (8) and (9) are fed with compressed air from compressor (16) for agitation of the solutions. Neutralization process of rinsing water is monitored by pH meter (7). Precipitated mixture of non-soluble metal salts is accumulated in precipitator (10) and is to be buried. Neutralized rinsing water passes through mechanical filter (11) and back osmosis system (12), after which it could be generally returned into technological cycle for primary washing of graphite. Waste water from system (12) goes to ion exchanger (15) and either returns into technological cycle for purification and washing of graphite or departs into sewerage.

Thoroughly washed graphite is deprived from water in centrifuge (13) with periodical dilution of product with warm distillate and alternation of high and low rate of rotation. Then, product is dried in drying oven (14) at 300 C.

The laboratory demo line for acidic treatment of kish graphite implemented at KNUTD is shown on Fig I-3.1.2.

Fig I-3.1.2. The laboratory demo line for acidic treatment of kish graphite assembled in KNUTD.

I-3.2. Selection of ready-made equipment for graphite pilot production with throughput rate of 100 ton per year

Fig I-3.1.3. Steel enameled reactor with anchor agitator

Particular consideration deserves the question of selection of industrial equipment for pilot production of graphite. Thick-walled glass reactor with stirrer and heater (e.g., Simax, Czech Republic) is the best for acidic treatment. This one prevents any extra contamination including that from contact with metals in aggressive media.

Though, disadvantage of such reactor is its fragility, which constitutes certain danger in industrial environment. Therefore, steel enameled reactor with anchor agitator may be used alternatively (Fig I-3.1.3).

Such the blocks are serially produced, for one, at the ‘Krasny Oktyabr’ (Red October) plant of chemical engineering in Fastiv, Kiev region, Ukraine. These are oriented to operation with aggressive media including acids. No doubts, enamel covering inner walls of reactor is proof to action of hydrochloric acid.

Anchor agitator is made of stainless steel and its durability in concentrated hydrochloric acid gives rise to doubt.

By special order, agitator might be covered by some polymer (e.g., polyethylene) that excludes a possibility of corrosion of agitator in such aggressive medium.

For final choice between glass reactor and steel enameled one, the latter is to be tested with concentrated hydrochloric acid. *The better way is to request the specifications from manufacturing plant (M.S.)*

Table I-3.1.3 represents a standard stock-list of the ‘Krasny Oktyabr’ factory on this kind of produce.

Table I-3.1.3. Specifications of steel enameled reactors fitted with anchor agitator

Marking	Working volume, m ³	Jacket volume, m ³	Type of drive	Overall dimensions	
				H	D
ASEonv 1.0-2-02	1.0	0.21	V112-1.5-50-2P	3060	1000
ASEonv 1.6-2-02	1.6	0.222	V140-3.0-50-2P	3370	1200
ASEonv 2.5-2-02	2.5	0.5	V140-3.0-50-2P	3590	1400
ASEonv 4.0-2-02	4.0	0.533	V180-5.5-50-2P	4115	1600

For set productivity of 100 tpy and as calculations show, it is enough to choose the smallest reactor with working volume of 1 m³.

Washing of graphite after acidic treatment remains the bottleneck of the whole process by duration. Previously, we supposed that press-filter could have been used at working conditions. The P-154 Project even provided for assignment of press-filter from SGC, Chicago to Kiev in order to accelerate the process of graphite washing and overcome this bottleneck. Nevertheless, more thorough analysis of the working principles of such equipment and testing on the models of press-filter made at KNUDT brought us to giving up the use of this equipment. This equipment does not fit principally for good washing of graphite powder because, at pressing, graphite powder is compressed into porous plates (so called, cake) and there are a lot of non-swept admixtures of metal chlorides in the pores of such plates. The plates is to be ground into powder for repeat washing and for thorough washing mentioned above such operation must be done multiply; this is inappropriate neither technically nor economically.

In laboratory environment, we initially washed graphite on Büchner funnel and then, for better efficiency, by the instrumentality of metal filters with anticorrosion overcoat working under vacuum.

In industrial environment, washing of graphite is to be done on nutsch filter (Fig I-3.1.4) and much better on Druckfilter (*German*) with stirring (Fig I-3.1.5).

Fig I-3.1.4. Steel enameled nutsch filter with underpressure

Fig I-3.1.5. Steel enameled Druckfilter with elevating stirring device

‘Krasny Oktyabr’ factory of chemical engineering in Fastiv, Kiev region, Ukraine produces such output in sufficient assortment.

We recommend the following standard equipment of the factory for throughput rate of 100 tpy.

Steel enameled capacitive Druckfilter with elevating stirring device is assigned for filtration of mordant matters. It has mechanical discharge, elevating stirrer, flat grid, body and bottom jackets, up and down movement of bottom with grid for replacement of filter cloth. It is completed with electrics in normal and blast-proof versions.

Specifications of chosen device

Marking	Filtration surface, m ²	Volume of		Weight, kg	Overall dimensions	
		suspension receiver, m ³	filtrate collector, m ³		H	L
Filter SEo 1.0-12-01	1.0	1.2	0.5	2960	3585	1735

Steel enameled nutsch filter with underpressure

Specifications of chosen device (chosen version typed in bold)

Marking	Filtration surface, m ²	Volume, m ³	Weight, kg	Overall dimensions		
				L	B	H
Filter DSEov 0.2-11-12-01	0.2	0.062	300	1610	682	815
DSEov 0.4-11-12-01	0.4	0.19	610	2100	930	1020
DSEov 0.8-11-12-01	0.8	0.82	1250	2830	1268	1880

Metal filter with anticorrosion overcoat and under vacuum tested in structure of KNUTD laboratory unit is actually a laboratory prototype of nutsch filter. Druckfilter seems to be much more convenient industrial device for graphite washing because it has elevating stirrer, which could intensify the washing process.

Subject to recommended industrial equipment, process flowsheet for single-stage purification of graphite looks as on (Fig I-3.1.6); deployment of Druckfilter makes unnecessary use of reactor (3). Druckfilter (6) assumes its functions.

Fig I-3.1.6. The process flowsheet single-stage purification of kish graphite

1 – distiller; 2 – storage tank for distilled water; 3 – reactor for acidic treatment; 4 – drying oven; 5 – distilled water heater; 6 – Druckfilter; 7 – pump for pushing a liquid through graphite being washed; 8 – tank with neutralizer; 9 – filtrate storage; 10 – pH meter; 11 – precipitator; 12 – back osmosis water purifier; 13 – centrifuge; 14 – drying oven; 15 – ion exchanger.

The proposed scheme requires additional checking, testing, and working out of process modes particularly of neutralization and waste water purification.

I-3.2. Study of the samples of materials that have been purified at KNUTD

At the developed demo line following two technological schemes, we purified the samples of kish graphite with ash content of 95%, which were sent from Donetsk:

- 1) single-stage (treatment by hydrochloric acid);
- 2) three-stage (successive treatment by hydrochloric acid, by alkali at middle temperature, and by nitric acid).

The results have shown that already after one stage of treatment in hydrochloric acid, purity of graphite powder generally fits the requirements of battery trade both by total ash content (0.5-0.6%) and by content of individual mineral admixtures.

Fig I-3.1.7. Microphotograph and chemical composition of impurities of kish graphite upgraded by Donetsk team up to 95%C

Fig I-3.1.8. Microphotograph and chemical composition of impurities of kish graphite purified at KNUTD up to 99.5%C

Whereas iron impurities prevail in initial sample (Fig I-3.1.7), after acidic treatment impurities of silicon and aluminum dominate (Fig I-3.1.8).

These conclusions were confirmed by the results of testing of corresponding samples in USA.

Fig I-3.1.9. Microphotograph and chemical composition of impurities of kish graphite purified at KNUTD down to 0.5% of ash content in single-stage process (data of SGC).

Table I-3.1.1. What was Achieved by IPOCC and KNUTD in Purification (SGC data):

Graphite:	NATURAL CRYSTALLINE FLAKE GRAPHITE					KISH GRAPHITE	
	(2939APH, SG reference material)	Feed at IPOCC (Zavaliy Flake) - MKKZ	IPOCC Cl ₂ -purified, SR12728 #2)	IPOCC CCl ₄ -purified 251007, SR13080	flake KNUTD1007-5 (SR12863) - 3 stages of purif.	Kish upgraded in HCl (1 stage) at KNUTD, sample 012909, SR13178	Kish upgraded in 3 stages at KNUTD, sample 013009, SR13178
LOI, %	99.95	95.2	99.9+	99.99	99.991	99.57	99.75
Element							
Al	<30	1337.8	13.17	9.13	2.16	54.9	10.6
As	<1	8.45	0	0.27	0.3	0.66	0.21
Ca	<100	156.3	5.18	2.30	6.8	30.18	15.9
Co	<3	1.56	<0.01	0.07	<0.01	0.08	0.01
Cr	<5	7.9	0	<0.01	0.09	6.62	2.28
Cu	<5	52.2	<0.01	<0.01	0.47	1.79	0.31
Fe	<150	2380.4	1.22	0.75	19.92	85.3	29.33
Mo	<3	49.9	13.97	7.40	0.06	0.07	0.02
Ni	<5	4	0	<0.01	0.31	0.08	<0.01
Pb	<5	1.83	0	0.01	<0.01	0.85	<0.01
Sb	<2	0.97	0	<0.01	<0.01	0.13	<0.01
Si	<200	9.49	2.53	1.18	0.54	9.43	0.17
Sn	<5	1.2	0.12	0.70	<0.01	<0.01	<0.01
V	<10	28.6	0.18	<0.01	0	2.16	0.21

For reference, ICP on Fe for feed material was: 23,963 ppm (SR 13139).

As one could see, only content of chrome and aluminum impurities in sample #1 exceeds the requirements of battery trade.

Both flake and kish graphite samples obtained after three-stage purification show bare quantity of all admixtures (Table I-3.1.1.). Such graphite could find its application in manufacture of artificial diamonds and in other new for SGC potential markets. However, working time for obtaining of the sample #2 are 5-6 times higher due to abrupt increasing of duration of the process of washing especially after alkaline treatment.

Specifically, while cycle of single-stage treatment of 1 kg of kish graphite may be completed in day and night, full cycle of three-stage treatment of 1 kg of same material is lasting for 5-6 calendar days.

It is clear that perfection of single-stage process of acidic treatment is more reasonable for graphites directed to battery trade than purification of graphite by three-stage scheme.

During the nearest six months, KNUTD team will endeavor to solve the problem of chrome and aluminum removal to meet the requirements of battery market using only single-stage acidic treatment, if concerted additional funding is granted.

At the expense of this funding, full scheme of neutralization of sewages and recovery of wastes of the processes of chemical purification will be developed too. The problem will inevitably demand its solution at scaling of production.

I-3.3. A patent disclosure for chemical purification of graphite

Ukrainian version of invention application executed with accordance to the Ukrainian patent legislation and is set below.

IPC⁷ C01B 31/04

The Method of Chemical Purification of Graphites

The invention is applied to chemical industry and may be used for purification of graphites from admixtures and predominately for purification of graphite powders, which are formed, e.g., blast-furnace production (kish graphite).

Graphite powder (kish graphite) is of little avail for immediate industrial use because it is strongly contaminated by side products of blast-furnace production. Therefore, it is subjected to preparatory washing (flotation) and magnetic separation, which release it substantially from slag and iron-containing particles. However, even after that treatment, graphite powder has relatively high ash content (~5 %) and makes up flat rounded particles with size, which usually is no more than 1 mm. On the surface and inside the particles, there are a lot of fine-dispersed particles of impurities containing up to 97% of iron. Besides, they contain silicon (~0.79%), aluminum (~0.63%), magnesium (~0.6%), sodium (~0.5%), calcium (~0.2%), and other elements. Such nature of impurities is connected with the features of the processes of graphite generation in blast-furnace process.

Further physical-mechanical purification of graphite powder is not effective. So, use of chemical purification is expedient for final treatment of graphite powder; this operation in the first place, is headed to decomposition of iron and aluminum compounds containing inside of the graphite grains as ferrosilicates and aluminum ones. Concomitant operations are to exclude the products of chemical reactions out of the structure of graphite material.

Among the known methods of chemical purification of graphites, the most extensively used are acidic, alkaline, and combined – acidic-alkaline methods as well as thermo-purification in chlorine atmosphere [Fialkov A.S. Carbon-graphite materials. – Moscow: Energy, 1979, (in Russian)]. Depending on initial ash content and type of admixtures, one of the known methods is used. As for graphites with predominate content of iron, acid treatment is the most efficient, thus iron transforms into salts of corresponding acid and those are removed at water washing.

A known method of chemical purification of graphite lies in the treatment of graphite bulk by sulphuric or hydrofluoric acid and next following washing by water [GB Patent No. 7921, 1901]. However, the method is not efficient enough since it does not allow indispensable degree of graphite purification (at least up to 99.95% of carbon). Investigations show that use of sulphuric acid contaminates graphite sufficiently with sulphur. Analysis of ash residue indicates that after purification by these acids, graphite has relatively high remainder of such elements as Al, Fe, Si. Apparently, intrusion of an acid in by the graphite particle, where impurity is blocked from every quarter, is hampered very much. Besides, some impurities may be fully encapsulated either in silicates or in silicon oxide. However, decomposition of silicates by hydrofluoric acid makes this relatively simple method to be dangerous environmentally.

One more method of chemical purification of graphite is known; it is based on bulk graphite treatment by hydrochloric acid with further washing by water, additional treatment by alkali or soda at heating to 1050 C, and final washing by water with addition of an acid [FR Patent No. 1145024, 1915]. Disadvantage of the method is a generation of coking products in the course of alkali treatment; those are badly soluble and clog technological equipment.

Also, well-known method of chemical purification of graphite consists in mixing of graphite powder with acid, water washing of reaction mass, and further drying [RU Patent No. 2141449 C1, IPC C01B31/04, 1999]. Besides, a known method includes baking of graphite powder with water alkali solution at 350 C and washing of graphite by pulse counterflow of diluted nitric acid.

Disadvantage of the method is durability of technological process of purification due to consolidation of baking products at cooling; those are hard to be crushed and dissolved in acid. Owing to, graphite is to be repeatedly washed at first by diluted acid and then by water. In addition, sizable material costs are required for purchasing of expensive equipment (furnaces with mechanical stirring, pulsating columns, etc.).

In the basis of the invention, there is prescribed the task of creation of such method of chemical purification where introduction of new operations and different conditions of their execution could provide speeding-up the process of graphite purification and reduction of costs for its realization.

Assigned task is solved by the method consisting in mixing of graphite powder with acid, washing of reaction mass by water, and further drying, and according to invention, before acidic treatment, graphite powder is additionally heated to 300 C, mixed with concentrated acid, and then result suspension is vacuumized during 40-45 minutes. The end product is filtered and dessicated.

In so doing, mixing of heated powder is performed with concentrated hydrochloric acid, the mixture is continuously stirred and heated additionally, e.g., in reactor with mechanical stirrer and heat-exchanger.

Besides, filtration of reaction product is made with adding of distilled water heated to 70-80 C, e.g., on a nutsch filter achieving both pH value of rinsing water equal 7 and conductivity value equal to that of initial distillate.

It is expedient to dessicate filtrated product by rotation with variable speed, e.g., in centrifuge with intermittent dilution of product by warm distillate, rotating with low speed, and following dewatering of product at maximal rotation.

Preliminary heating of graphite grains, which may contain enclosed particle of admixture inside, up to 300 C provides decrepitation of the grain due to difference of factors of thermal expansion of graphite and admixture. Consequently, concentrated hydrochloric acid penetrates deep into the grain. Cooling of graphite during intermixing with acid also promotes its penetration into the matrix of initial material and further into graphite pores. At subsequent vacuumizing, concentrated hydrochloric acid fills graphite pores entirely. In order to intensify the process, graphite-acidic suspension is kept under vacuum for 40-45 minutes.

Continuous stirring of reaction mass with additional heating within reactor speeds up chemical reactions with admixtures. Filtration of reaction products with addition of distilled water heated to 70-80 C promotes elution of salts generated in chemical processes from graphite pores. Dewatering of graphite powder by centrifugal forces at its rotation with variable rates and intermittent dilution by warm distillate allows decreasing of consumption of distillate and obtaining wet graphite with acceptable moistness. Admixtures from graphite pores are removed to necessary level providing residual ash content no more than 0.5-0.7%. Duration of purification is of 24 hours. Thus, the process of graphite purification does faster, and material costs are lowered.

Proposed method of chemical purification of graphite powder is realized using standard equipment of chemical technological industry.

The draft bellow shows the example of technological scheme of chemical purification of graphite.

In the scheme: 1 – storage bin for graphite powder that was physical-mechanically pretreated; 2 – heating chamber; 3 – steam generator; 4 – distiller; 5 – tank-collector; 6 – water heater; 7 – reactor with stirrer and heat exchanger; 8 – reservoir for hydrochloric acid; 9 – vacuum pump; 10 – nutsch filter; 11 – centrifuge; 12 – collector of dry graphite powder.

Chemical purification of graphite is performed as follows.

After physical-mechanical treatment, graphite powder is collected in storage bin (1) where from it is fed into heating chamber (2) by portions. Heating of graphite is made by steam from steam generator (3). Distilled water from multichamber distiller (4) working by the principle of steam compression is a source of steam in steam generator (3). Purified water from distiller comes into tank-collector (5), which feeds steam generator (3) and water heater (6). Water heater vessel has a jacket and enables storage of heated distilled water.

Graphite powder heated to 300 C comes from chamber (2) to reactor (7) where it is continuously intermixed with concentrated hydrochloric acid coming from reservoir (8).

In order to sustain high temperature of reaction mass, reactor (7) is equipped with spiral heat exchanger supplied by steam from steam generator (3). Simultaneously with stirring, vacuum pump (9) evacuates air from reactor (7). By vacuumizing of suspension, acid penetrates through all the pores and reacts with admixtures. Electric drive of stirrer of reactor (7) provides intensive intermixing of suspension with rotation rate of 115-120 rpm during 40-45 minutes.

On finishing of acidic treatment of graphite, suspension is poured out on nutsch filter (10) for prior washing and separation of graphite powder from products of chemical reactions. Prior washing is made at first by back osmosis purified water from return cycle to achieve pH value of 5-6 and then by distilled water heated to 70-80 C from tank-collector (6) to achieve pH value equal 7 and conductivity value equal that of initial distillate. Final washing and dewatering of graphite powder is made in centrifuge (11) where wet graphite is loaded after filtration. For full purification and dewatering of graphite, it is periodically diluted by warm distillate, and centrifuge is rotated with low speed. Dewatering of the powder is performed at maximal rotation. Washing is made until pH value is equal 7 and conductivity value is equal that of initial distillate. By altering operation of centrifuge (11), distillate and admixtures are removed from graphite almost fully; this provides residual ash content no more than 0.5-0.6% at initial ash content of ~5%. Dewatered powder is amassed in collector (12).

Thorough preliminary flotation and magnetic separation of initial material are very significant for chemical purification of graphite; these allow more inexpensive separation of mineral inclusions that practically yield to no decomposition by chemical action. Therefore, after preliminary physical-mechanical treatment, graphite could be purified chemically during no more than 24 hours at possible additional expenditures no more than \$400 per ton (counting on efficiency of 100 tpy) obtaining hereby pure enough and inexpensive similar to natural graphite.

Atomic absorption analysis of samples of kish graphite purified by supposed method has shown appropriate residual content of metal inclusions. Thus, content of impurities does not exceed the following values (ppm): iron ~17.1;

aluminum ~16.8; nickel ~0.8; chrome ~1.2; copper, molybdenum, lead, vanadium – less than 0.1. Thereby, supposed method of chemical purification of graphite provides high enough degree of graphite purity (99.5%) and about tree times decreasing of consumption of electricity, distilled water, reagents, and other consumables. Total time and labor expenditures are decreased too. Graphite purified by the method may be directly used for battery making. Due to reducing of the admixture content in graphite, self-discharge value decreases substantially, and lifetime increases for tractive (Ni-Cd and Ni-Fe) accumulators and primary Zn-Mn batteries, which use graphite as electro-conductive dope to active materials.

The Method of Chemical Purification of Graphite

Patent claim

1. The method of chemical purification of graphite consisting in intermixing of graphite powder with acid, washing of reaction mass by water, and further drying, wherein graphite powder, before acidic treatment, is heated to temperature of 300 C, mixed with concentrated hydrochloric acid, and result suspension is vacuumized over 40-45 minutes. Product is filtered and dewatered.
2. The method of claim 1, wherein intermixing of heated powder is carried out with hydrochloric acid, mixture is continuously stirred and additionally heated, e.g., in the reactor with mechanical stirrer and heat exchanger.
3. The method of claim 1, wherein filtration of product is carried out, e.g., on the nutsch filter with washing at first by back osmosis purified water from return cycle to achieve pH value of 5-6 and then by distilled water heated to 70-80 C to achieve pH value equal 7 and conductivity value equal that of initial distillate.
4. The method of claim 1, wherein final washing and dewatering of filtered out product is carried out by its rotation with variable speed, e.g., in centrifuge with periodical dilution of product by warm distillate, rotation with low speed with further dewatering of product at maximal rate of rotation.

Composite author from sides of Ukraine and USA is planned to be finally specified during forthcoming Site visit to KNUTD in June, 2009. During the visit, we plan also to discuss the status of application, algorithm and time constraints of its filling to patent authorities of Ukraine and USA, and to prepare a business document, which will guide future commercial relationship between SGC and KNUTD.

CONCLUSIONS

1. KNUTD team has completed the making and testing of the laboratory demo line for single-stage purification of kish graphite (acidic treatment) including conceptual workup of the question of neutralization and sewage treatment.

2. Using the single-stage of acidic treatment, one could be successful obtaining 99.5%C graphite, which virtually fits the requirements of battery trade (excluding some excess of aluminum and chrome impurities).
3. Using of full cycle of chemical treatment for kish graphite enables one to obtain high-pure graphite with carbon content no less than 99.9% that offers the challenge of entries such markets as manufacture of artificial diamonds, etc.
4. The question is worked out on using of industrial equipment for commercialization of the process of single-stage purification of kish graphite (acidic treatment).
5. The patent disclosure for chemical purification of graphite has been drawn up.

I-4.1 Pilot EC[®] facility performance analysis

The quality of technological processes and, correspondingly, the quality of products manufactured with their use are much determined by the maintenance of parameter stability of the processes. In particular, the service of the pilot Electroconsolidation (EC[®]) facility has revealed some bottlenecks in its operation. The main of them are the support of stable temperature control over the EC[®] process and the choice of efficient elastically compressed medium used for transmitting pressure and temperature to the products.

I-4.1.1 Activities aimed at solving the temperature control problem.

A reliable temperature control of technological processes conducted at the EC[®] facility presents a rather complicated problem. This is explained by the presence of high heating rates, electrical and magnetic fields, powder filling, pressures. For temperature control we have chosen the method of X-ray monitoring of melting heat sensors and the method of indirect temperature control by thermocouples mounted in the walls of a graphite die assembly.

The melting heat sensors are used to determine the temperature inside the products. The temperature values in the given section can be estimated from the commencement of liquefaction of the heat sensor placed in it. The material of heat sensors is chosen so that that it should melt at the given temperature.

The heat sensor monitoring is conducted with the help of X-ray radiation. In this case, the X-ray detector must have a high resolving power and must be protected against direct X-ray radiation.

As an alternative, one can use standard X-ray apparatuses that comprise an X-ray imaging device (XRID). The main disadvantage of these systems is their high sensitivity to external magnetic fields. Since the objects under study are heated by passing high electric current through them, there exist high constant electromagnetic fields, the shielding of which is a rather time consuming task.

Instead of XRID, full-scale amorphous silicon matrices can be used. However, the shortcoming of these matrices is their high cost and insufficient radiation resistance.

For a more exact control of heat sensor melting temperature, we have chosen the registration technique, which makes use of the detectors based on special charge-coupled devices (CCD). Such a detector is placed on the extension of the ray going from the focus of the X-ray source and passing through one of the heat sensors. So, each of the detectors can “see” only one of the heat sensors.

One of the advantages of the detectors is their low cost. So, one can afford making several such detectors for the receiving device, and the heat sensors can be arranged in the corresponding sites so that the images produced could reach the receiving devices.

The second advantage of the detectors is their high radiation resistance due to a very small thickness of the crystal. For this reason, direct X-rays not absorbed in the luminophor can pass through the CCD crystal without absorption.

The third advantage of the system under consideration consists in low light losses. Since the luminophor is situated in the immediate vicinity of the CCD crystal, practically all of the optical-band photons that were produced in the luminophor during absorption of X-ray quanta by the latter reach the CCD.

Figure 1 shows the basic diagram of X-ray optical conversion and registration used at the EC[®] facility.

When tuning up the radiographic temperature control equipment and working with it, we ran into the problems of stable operation of X-ray sensors-detectors. Their readings were influenced by their location relative to the die-assembly and by the technological process conditions (range and rate of rise in the current flowing inside the die assembly).

A series of experiments have permitted us to determine the appropriate sensor-detector stations and to correct the operating conditions of the X-ray source. When tuning up the facility we have used the heat sensors made from the following materials:

- Lead (melting point - 293°C);
- Aluminum (melting point - 660°C);
- Copper (melting point - 1083°C);
- Nickel (melting point - 1455°C);
- Iron (melting point - 1539°C);
- Titanium (melting point - 1668°C);
- Zirconium (melting point – 1852°C);
- Boron (melting point - 2100°C);
- Hafnium (melting point - 2200°C).

Figure 2 illustrates the process of neutron-absorbing pellet production under a stable operation of X-ray imaging equipment.

Fig. 2. X-ray imaging support of the process of neutron-absorbing pellet production: a – beginning of experiment, b – commencement of liquefaction of Pb-base heat sensors (1), c – completion phase of experiment (the Pb-base heat sensors have fully melted and merged in a graphite powder; the effect of Cu-base heat sensor (2) melting can be seen; the Ti-base heat sensors have underwent no changes). 1 – Pb-base heat sensors, 2 – Cu-base heat sensors, 3 – Ti-base heat sensors.

The resulting experimental samples showed a wide spread in their physical characteristics, and the repeatability of results was periodically absent. Therefore, we have decided to conduct work at production of heat sensors based on binary alloys. We have analyzed a number of alloys that seemed most suitable for the technological processes realized at the EC[®] facility. From among the systems considered, the Al-Mo alloy has appeared most promising, as it fully overlapped the temperature range from 660°C up to 2700°C.

I-4.1.2 Effects associated with elastically compressed medium.

As the technological EC[®] process is conducted, the pressure is formed under the action of mechanical compression of the powder that fills the working part of the die assembly. In the experiments, we have used the powders of 310 to 400 μm in particle size, prepared from MPG-6 Type graphite, pyrolytic graphite, and the graphite and boron nitride powder mixture.

The undertaken experiments have demonstrated that the flow properties of the powders used were unsatisfactory. This leads to the fact that the deformation of products along the direction of compressing force application is substantially heavier than the deformation in the plane of perpendicular to this direction. For example, in the process of hot pressing of cylindrical samples the relative change in their height ranged between ~38 and 50%, while the relative reduction in the diameter varied from 10 to 15%.

In view of this, it is necessary to conduct work on further optimization of the composition and structure of graphite powders. Of particular interest in EC[®] processes is the use of graphites manufactured by the Superior Graphite Company.

I-4.2 Improvement of absorbing materials

In recent years, especially after the known accidents at NPPs, requirements have grown to absorbing materials and other reactor core elements when operated in emergency situations, connected, in particular, with power surge and raise of temperature. Therefore, at present, the specialists consider it unreasonable to use low-melting absorbers. Thus, at PWR reactors of the West countries, activities are undertaken to replace the 80%Ag-15%In-5%Cd metal alloy, which has the melting temperature of about 800°C, by hafnium alloys or by hafnium diboride.

When in service, the control elements in the reactor are moved in the core. In the case that the dimensional instability arises, the mobility of the regulating elements is violated, this generally causing the reactor shutdown. The loss of sealing and failure of control elements are impermissible. The washing-out and ingress of absorbing materials into the primary

coolant circuit of the reactor upset its neutron-physical characteristics. In this connection, the absorbing materials must have a high radiation resistance and maintain their shape, dimensions and integrity during their service in the reactor.

The main factor that determines the working ability of absorber rods (AR) of the control and protection system (CPS) in WWER-1000 reactors widely used in Ukraine is connected with the radiation resistance of ARs and their material constituents. The design of ARs and the conditions of their work in the reactor specify a very high nonuniformity of neutron radiation action on the ARs in height. The bottom ends of ARs most suffer from this action, while in essence, it is the radiation resistance of AR bottom ends, about 500 mm in length, that is responsible for the operational capability of CPS AR as a whole. The main factors that limit the working capacity of boron carbide-based ARs are connected with the burnup of the absorbing isotope ^{10}B , that leads to gas production and AR swelling.

In consequence of reactor irradiation, helium is produced and accumulated in boron carbide. This inevitably results in the formation of gas pores, in cracking and breakdown of a compact AR. Besides, the particles that result from nuclear interaction and have a high kinetic energy (above 1 MeV) have a free path (up to 3 μm) in the material. A comparatively long path of the particles causes substantial damages of the crystalline structure down to its full amorphization as early as at the initial stage of reactor irradiation. Under irradiation in the thermal neutron spectrum, the reactions on ^{10}B nuclei proceed nonuniformly in the cross section of the AR. As a result, great differences are observed in material swelling and between the stress fields. The accumulation of gaseous nuclear reaction products is accompanied not only by volumetric changes, but also by degradation of practically all operationally important properties – thermophysical, mechanical, chemical. It should be specially emphasized that this is typical of all conceivable (n, α) absorbers (ceramic, dispersive, metallic), thereby permitting us to characterize the given class of materials as a non-resistant to radiation.

On the other hand, under the action of fast neutrons the plastic properties of the shell get degraded. Taken together, the mentioned processes are capable of causing a severe deformation of the AR shell and to its failure.

A further improvement in the safety and reliability of CPS AR operation of the Russian reactor WWER-1000 involves the transition to alternative AR designs with combined absorbers. The top part of the shell of these ARs is filled with boron carbide powder, and the bottom part is filled with the absorbing material, which enters into the (n, γ)-reaction with neutrons. The ARs, for which the dysprosium titanate powder is used in the bottom part, and the nickel alloy EhP-630U (Ni-42 wt.-%-Cr-1 wt.-%-Mo) is used as a shell material, have been manufactured by the Moscow Polymetal Plant since 1997 [1-3]. In the long term, in order to improve the physical efficiency of CPS ARs, it is planned to replace the mentioned powder by dysprosium titanate pellets. The use of dysprosium hafnate as an (n, γ)-absorber is expected to be very efficient [4, 5].

In (n, γ)-absorbers, the gaseous products of nuclear reactions do not accumulate. The main neutron irradiation effect on them manifests itself mainly in the formation of point radiation defects and in the evolution of their configurations.

The process of neutron irradiation is accompanied by generation of focused atomic collisions in the densest crystallographic directions, which form dynamic crowdions displacing interstitial atoms. The conditions of focused dynamic crowdion formation include the presence of regular close-packed atomic chains, “focusing lenses” formed from surrounding atoms, etc., in the structure. These conditions are realized most readily in substances having the most regular, close to ideal, crystal structures. On the contrary, in substances having a most random structure, the conditions for focusing dynamic crowdions can be realized with the least probability. This means that in the crystal with a high degree of atomic order in the structure and a great number of close-packed atomic layers and directions there is a possibility of stable radiation defect accumulation. And, on the contrary, in crystals with perturbed focusing directions in the structure, the overwhelming majority of arising defects recombines without formation of stable radiation defects. It is just the materials with this type of the structure that show the highest radiation resistance.

As evidenced by the computer simulation data and the results of material irradiation experiments, a high defocusing ability is exhibited by structural stoichiometric vacancies in the crystals having the fluorite-type structure or its derivatives. For example, sesquioxides of rare-earth elements (including Eu_2O_3 , Gd_2O_3 , Y_2O_3) possess an anomalously high radiation resistance.

In other words, the fluorite-type crystal structure is most stable and low-sensitive to reactor irradiation. It is typical of many oxygen and complex-oxygen compounds of rare-earth elements. In particular, the fluorite structure can form in such absorbing materials as dysprosium titanate and dysprosium hafnate. It has been established that there is a direct relationship between the coordination number and the structure non-equilibrium. The less is the coordination number of the substance before irradiation, the poorer is the equilibrium of the structure and the lower is the material sensitivity to radiation damages that lead to volume changes.

The second direction in improving the material resistance to irradiation effects is the creation of nanostructures in the materials. With crystallite fragmentation the mean coordination number will decrease. For example, to reduce the mean coordination number by 5 to 10 %, it is sufficient to split the crystallites down to a size of 10.0 to 20.0 nm. In this case, in the process of phase transitions new crystalline structures will be formed, where atoms have a lower coordination number, and what is of most importance, there is an appreciable rise in the surface energy that governs the properties and behavior of the material. Thus, it appears rather promising to apply nanotechnologies for the materials that are subjected to great volumetric changes under reactor irradiation.

On the basis of the above-given ideas about the behavior of complex-oxygen compounds of rare-earth elements under reactor irradiation, one can point out three groups of materials: i) materials with the fluorite structure in the initial state; ii) materials with pyrochlore, rhombic and other structures that change to the fluorite structure under reactor irradiation; iii) all other materials. In the motion from the first group to the third one, the material swelling, as a rule, increases (Fig. 3).

Fig. 3. Molecular volume variations of dysprosium titanate crystal structures: α - rhombohedral lattice, β - hexagonal lattice, F - fluorite, P - pyrochlore.

Thus, for creation of promising absorbing materials it is of importance to solve the following three tasks:

- high-density pellet production;
- realization of a radiation-resistant structure, e.g., fluorite structure;
- creation of high-efficiency technology.

These tasks can successfully be carried out, in our opinion, by means of the EC[®] technology.

I-4.3 INVESTIGATION OF ABSORBING PELLETS

I-4.3.1 Lines of investigations.

As for now, we investigate the influence of hot pressing conditions with the use of the EC[®] technology on the density and structure of absorbing pellets prepared from dysprosium titanate and dysprosium hafnate.

I-4.3.2 Pellet production scheme.

The pellets were produced by the previously developed flow scheme, which includes the following operations:

- weighing of powder constituents;
- mixing of powders;
- introduction of a binder;
- product forming;
- elimination of the binder and presintering of products;
- hot pressing by the EC[®] technology ;
- mechanical working;
- control and investigation of properties of finished products.

The absorbing pellets were prepared from the following mixture compositions:

After weighing and dosing, the powders were mixed in a ball mill "Pullverizette-6" at a rate of 100 rev/min for a period of 8 hours. Hard-alloy volume capacity and balls were used to mix the powders. Then, a binder, being a mixture of paraffin and petrolatum, was introduced into the powder mixtures, and the products of given geometrical dimensions were formed. After elimination of the binder and presintering of products, the last ones were subjected to the treatment by the EC[®] technology. At this process stage, the products were placed into the graphite powder, and hot pressing in vacuum of ~ 1Pa was conducted. Hot pressing was performed at temperatures of 1050, 1250, 1450, and 1650°C. The compacting pressure was equal to 45 MPa. The products were held under pressure for 20 minutes. The heating of products was carried out at a rate of 16°C/min, the cooling operation was performed at a rate of 10°C/min.

I-4.3.3 Results of absorbing material analysis.

The density of absorbing pellets was measured by the method of hydrostatic weighing. The results of determining the density as a function of hot pressing temperature are presented in Fig. 4.

Fig. 4. Dysprosium titanate (a) and dysprosium hafnate (b) sample densities versus temperature of pressing by the EC[®] technology at a pressure of 45 MPa and dwelling time of 20 min at pressing temperature.

The present results indicate that the density making 0.97 to 0.98 of the theoretical value is attained with dysprosium titanate and dysprosium hafnate pellets beginning with hot pressing temperatures of 1400°C (Fig. 4a) and 1600°C (Fig. 4b), respectively. The maximum density values attained in these experiments were found to be 7.2 g/cm³ and 8.7 g/cm³ for dysprosium titanate and dysprosium hafnate, correspondingly. A reduction in the EC[®] process temperature leads to a decrease in absorbing pellet density values.

X-ray diffractometry examination of pellets prepared from mixtures (1) and (2) was performed using the diffractometer DRON-1 in copper radiation with the Bragg-Brentano focusing. To cut off the characteristic radiation constituent K_β, a nickel selective filter was used.

The X-ray diffractometry data for dysprosium titanate samples produced by hot EC[®] pressing at pressure of 45 MPa with a pressing process time of 20 min have given evidence that at a temperature of 1050°C (Fig. 5a) the phase Dy₂Ti₂O₇ with a cubic lattice ($a = 10.12 \pm 0.01 \text{ \AA}$) is generally formed. A rise in the hot pressing temperature up to 1250°C led to a partial failure of the Dy₂Ti₂O₇ phase and to the formation of the Dy₂TiO₅ phase with a hexagonal lattice (Fig. 5b). At a pressing temperature of 1450°C, nearly a total decomposition of the Dy₂Ti₂O₇ phase was observed (Fig. 5c). At that, the content of the Dy₂TiO₅ phase increased. A further increase in the hot pressing temperature up to 1650°C resulted in the synthesis of the Dy₂TiO₅ phase with a hexagonal lattice in the entire volume of the pellets (Fig. 5 d). The crystal lattice parameters of the Dy₂TiO₅ phase were found to be $a = 3.63 \pm 0.01 \text{ \AA}$ and $c = 11.76 \pm 0.01 \text{ \AA}$.

Fig. 5. Diffractograms of dysprosium titanate pellets after hot pressing at 45 MPa for 20 minutes at temperatures: a - 1050°C; b - 1250°C, c - 1450°C, d - 1650°C.

The X-ray diffractometry data for dysprosium hafnate pellets produced by hot pressing with the use of the EC[®] technology at the above-mentioned operating conditions are given in Fig. 6.

Fig. 6. Diffractograms of dysprosium hafnate pellets after hot pressing at 45 MPa for 20 minutes at temperatures: a - 1250°C, b - 1450°C, c – 1650°C

According to the data shown in the figure, the synthesis of dysprosium hafnate takes place at EC[®] process temperatures close to 1450°C (Fig. 6b). Beginning with this temperature the Dy₂Hf₂O₇ phase with a cubic lattice ($a=5.25\pm0.01\text{\AA}$) is formed, the phase being related to the fluorite type of the structure.

A further increase in the electroconsolidation temperature up to 1650°C brought no change in the phase composition of the system (Fig. 6c), the crystal lattice parameter being in this case equal to $a = 5.24\pm0.01\text{\AA}$. An insignificant reduction in the lattice parameter of dysprosium hafnate with an increasing temperature of electroconsolidation may point to densification of the crystal lattice.

The X-ray diffractometry examination of the material of the samples that underwent the EC[®] process at a temperature of 1250°C has indicated that hafnium/dysprosium oxides constitute the major portion of its content. The Dy₂Hf₂O₇ phase was observed to form in small quantities.

I-4.4 pilot pellet batch production by the EC[®]

The dysprosium titanate/hafnate pellets were produced by the flow scheme presented in subsection 1-4.3.2. The treatment of the pellets by the EC[®] technology was realized in the die assembly, the design of which is shown in Fig. 7.

Fig. 7. External view of the graphite die assembly: a – die assembly and punches before fitting up; b – die assembly with a thermal shield and punches.

The die assembly had the following dimensions:

- height, mm 140;
- outside diameter, mm 108;
- working area diameter, mm 50;
- punch diameter, mm 50;
- punch height, mm 80.

Type MPG-6 graphite was used as an elastically compressed medium. The die assembly had stiffening ribs, 2 mm in thickness and 5 mm in depth, all along the entire height. They are intended for increasing the die assembly surface.

In the manufacture of products, the process of hot pressing was controlled with the help of the X-ray examination system RAP 150/300 and a thermocouple VR5-20, which was introduced through a ceramic pipe into the hole in the

middle part of the die assembly (Fig. 7). After the die assembly was filled with green pellets and a graphite powder, it was placed in a vacuum chamber of the EC[®] facility, and the process of pressing was conducted for 20 minutes at a temperature of 1650° C (Fig. 8).

Fig. 8. Arrangement of the die assembly with a shield in a vacuum chamber of the pilot EC[®] facility.

As a result of pressing, cylindrical dysprosium titanate pellets of density 7.0 to 7.2 g/cm³ and dysprosium hafnate pellets of density 8.5 to 8.7 g/cm³ were obtained (Fig. 9).

Fig. 9. Absorbing dysprosium titanate/hafnate pellets: a – X-ray imaging of the manufacturing process; b – external appearance after hot pressing and machining work.

I-4.5 SPECIAL FEATURES OF NANOMETRIC POWDER FORMING AND SINTERING

In the manufacturing technology of dental implants based on nanopowders, e.g., ZrO₂-3 mol.%Y₂O₃, an important place is given to the processes of forming and sintering of blanks.

It is known that the ceramics microstructure, formed in the process of sintering, is essentially dependent on the characteristics of the initial powder and on the microstructure of the uncured compact blank, i.e., on the molding technique.

The main physical characteristics of the molded product are as follows [7-9]:

- relative density;
- maximum pore size;
- uniform density;
- pore size distribution.

Reduction in the size of individual ceramic-powder particles causes a growing tendency for the last ones to form agglomerations, which account for a structural heterogeneity in an uncured molded blank. This particle size reduction appreciably intensifies the process of sintering [6]. There are the data [7] about an essential improvement in the agglomerating capacity and strength characteristics after additional densification of tetragonal zirconium dioxide powder blanks by a high-pressure fluid. The processing characteristics of finely dispersed powders can be improved through a short-time dry milling in a planetary mill. There is evidence that after a short (2 to 3 min) milling of Al₂O₃, Y₂O₃, and MgO powders, their bulk weight and the compact density increase, the sintering improves, and the linear shrinkage on annealing goes down [12]. It is worth noting that the samples, which underwent a 2-minute milling, show the maximum relative density and the minimum apparent porosity. As the milling time increases, the relative density decreases, and an apparent porosity appears, i.e., the sintering is impaired. The activation of sintering owing to short-time milling evidently takes place not only due to an increased compact density, but also due to a higher powder particle imperfection caused by densification-induced deformation.

In spite of the retention of a great specific surface area of the powder and an increase in the compact density, a too strong densification of particles appears adverse for sintering. Thus, the examination of the microstructure of annealed

samples has revealed that in the samples produced from the powders milled in the planetary mill for more than 3 min, there occurs the formation of areas of increased porosity. At the same time, aggregates of pore-free areas are observed. This is explained by the fact that the particle sintering inside the densified aggregates proceeds better than the sintering between the aggregates [13]. The ultimate flexural strength of oxide ceramics has its maximum at the powder milling time between 1 and 2 min, and when milling over 3 min the ultimate flexural strength of the ceramics remains practically unchanged.

The specific content of interagglomerate pores can serve as a quality criterion of particle packing in the compact. In the general case, an increase in the molding pressure reduces both the nonuniformity of pore-size distribution and the content of interagglomerate pores. However, at the pressure level corresponding to the onset of agglomerate breakdown, the nonuniformity of pore distribution in the compact can increase due to the formation of additional interagglomerate porosity and to the violation of agglomerate packing regularity [8]. In preparation of ultrafine powders (UFP) one can apply vibratory processing of the powder for obtaining “soft” agglomerates [10]. A combination of impact loads and shear loads at vibration substantially reduces the strength of coupling between separate elements of arising agglomerates, and the shape of the last ones is near to spherical at certain vibroprocessing conditions. After the processing, the compact density increases. A homogeneous “soft” agglomerate packing while the powder is compacted contributes to a homogeneous packing of particles in the blank and to the densification of the latter at sintering practically to the theoretical density.

There are several stages of agglomerated $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ sintering: neck formation between particles and intense shrinkage; appearance and growth of cracks, growth of pores and grains, shrinkage increase; deceleration of shrinkage and pore stabilization [6]. Dilatometer investigations have shown that the shrinkage curve for the sample prepared from nanocrystalline ZrO_2 powder is shifted by 200 K towards lower temperatures as compared to the curves for the samples made from coarse-grained zirconium dioxide. An active shrinkage of samples from ZrO_2 UFP and coarse-grained ZrO_2 begins, respectively, at 1100°C and 1200°, and ends at 1500°C and 1750°C, correspondingly [9, 11].

The process of sintering is substantially influenced by the additions introduced into the ZrO_2 -based UFP at the stage of their production. The additions may enter into a solid solution and form there vacancies, or may precipitate at grain boundaries, impeding recrystallization at the final stages of sintering and thus promoting densification [11]. Degradation in ZrO_2 sintering with an increasing quantity of stabilizer, as the temperature rises to the values exceeding the phase transition temperature in ZrO_2 , is caused by the fact that the structural defects, which arise at cubic solid solution formation, impede the diffusion processes that accompany sintering, i.e., the higher is the degree of ZrO_2 stabilization, the lower is its sintering [9].

The properties of ZrO_2 UFP-based materials are dependent on the rate of cooling after sintering. The quenching of samples provides a higher density rather than their cooling together with the furnace, this being apparently due to a reducing action of the outer layers of the material, which arises on quenching. Produced at low-temperature sintering (<1600°C), a high-density tetragonal zirconium dioxide, partially stabilized by Y_2O_3 , is characterized by high strength and fracture toughness values [13, 14]. However the properties of the material are much dependent on the temperature: as it rises up to 800°C, the strength and toughness sharply fall off.

CONCLUSION

The operation of the pilot EC[®] facility, developed and constructed in the context of the partnership project P-154 by the NSC KIPT jointly with the Argonne National Laboratory and the Superior Graphite Company, has demonstrated its capability for work, and also, the prospects for the use of the Electroconsolidation[®] process in a number of directions, e.g., for production of dysprosium titanate/hafnate absorbing pellets; milling bodies; products from nanodimensional powders, etc.

The operation of the pilot EC[®] facility has enabled us to detect some bottlenecks in its service. The main of them are the maintenance of stable control over the EC[®] process temperature, and the choice of an efficient elastically compressed medium used for transmitting pressure and temperature to the products. Ways of improving the EC[®] facility operation have been laid down.

The investigation of the structure and density of dysprosium titanate/hafnate pellets, produced by the EC[®] technology at different hot pressing temperatures, has permitted the optimization of their processing conditions.

At these optimized conditions it has appeared possible to produce dysprosium titanate pellets and dysprosium hafnate pellets of densities 7.2 g/cm³ and 8.7 g/cm³, respectively, this being 0.97... 0.98 of the theoretical value. Conditions of hot pressing by the EC[®] technology have been found, which provide the production of radiation-resistant structures Dy_2TiO_5 and $\text{Dy}_2\text{Hf}_2\text{O}_7$.

Relying on the literature data, analysis has been made to determine some special features of forming and sintering products from manometric powders.

It is pertinent to note that the development of the EC[®] process for manufacturing products from promising materials could be substantially advanced with the availability at our disposal of the graphite powder manufactured by the Superior Graphite Company.

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