기 술 전 망

High Pressure Liquid Jet Technology for Nano Particles Production

Marian Mazurkiewicz, Chang Kyu Rhee[a, *] **and Bogumil Weglinski**[b]
University of Science and Technology, Missouri-Rolla, USA and
Wroclaw University of Technology, Poland
[a]*Korea Atomic Energy Research Institute (KAERI), Korea,*
[b]*Wroclaw University of Technology, Poland*

Abstract Principles and historical background of high pressure liquid jet (HPLJ) technology is presented in the paper. This technology can be applied, among others, for production of nano particles. This target can be achieved in various type of disintegration systems developed and designed on the base of this technology. The paper describes principles of two examples of such systems: HPLJ- reactor, called also a linear comminuting system, HPLJ- centrifugal comminuting system, which prototypes have been manufactured. A linear mill, being high energy liquid jet reactor, has been developed and tested for micronization of various types of materials. The results achieved so far, and presented in the paper, show its potential for further improvement toward nano-size particle production. Flexibility of adjustment of the reactors and the mechanism of the process allows for the creation of particles with unprecedented rheology. The reactor can be especially suitable to micronize, mix and densify materials with a wide range of mechanical properties for various industrial needs. Presented prototypes of comminution systems generate interesting potentials toward production of nano particles. Their performance, based on up today research, confirms expected high efficiency of materials disintegration, which opens a new challenge for industrial applications. The paper points out benefits and area of possible applications of presented technology.

1. Introduction

In the macroscopic world, the physical properties of a material are independent of the sample size. However, when sample dimensions are made sufficiently small, the properties of the cluster of atoms must ultimately depart from those in the bulk and evolve as a function of size. This transition region where the "homogenous" bulk picture gives way to increasingly "atomistic" characteristic, as well as the structure of nano-meter size clusters of atoms, is an area of intense research interest, which target is production of nano particles.

Manufacture of nano particles is very important stage of nano technologies, because all essential their features are created at this stage. These include, not only the size and shape of nano particles, but also its rheology and stresses introduced during comminution. Industrial applications introduce additional factor-efficiency, influenced by energy consumption and production yield.

- Many various and differentiated methods are used for nano particles manufacture, but new, more efficient ones are still welcome. The following competing techniques can be distinguished at present:
- Mechanical Milling-produces micron-level particles but nano-level is time consuming and introducing a high level of contaminations.
- Chemical Precipitation-difficult to control particle size and shape, and produces hazardous waste solutions.
- Laser Ablation-has an extremely slow production rate of grams per day.

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*Corresponding Author : [Tel : +82-42-868-8551; E-mail : ckrhee@kaeri.re.kr]

- Thermal Spray-uses a slow process to produce micron-level particles, and some contamination takes place.
- Spray Pyrolysis-produces porous particles which are desirable mostly in ceramic applications.
- Laser Pyrolysis-has a slow production rate, but can be useful for iron oxides.
- Exploding wire-wide distribution of particle size, good production rate.
- Laser-Liquid-Solid Interaction-patent pending.

The authors of this paper took steps toward production of deep micronization by using an unprecedented tool-high energy liquid jet (HPLG). Conventional comminution technologies are both, energy intensive and inefficient. The mode of stress application to the particles is also a contributing factor to the inefficiencies of the standard comminuting equipment. Applying stress through the method of compression (particles are smashed and sheared off), which is the most common way, requires a much higher energy input than in the case where particles are fragmented by the tensile growth of preexisting internal flows or cracks which penetrates into the boundaries of the grains. Using liquid jet, the necessary internal tensile pressure is generated to propagate these preexisting cracks and micro-cracks.

Employment of high pressure liquid jet technology, which details are presented in this paper, creates a new way of nano particles production. Furthermore, rheology of obtained particles is univocal, due to phenomena taking place at this disintegration process.

2. Historical Background

Development of high pressure liquid jet technology was initiated parallelly at WUT (Poland) by Prof. Mazurkiewicz and in USA and UK in late 1960-ties.

Primary, this technology was focused for X and XY materials cutting as well as surface cleaning operation. An important step was made, when abrasive particles were added to liquid jet (1980). To make nozzle standing aggressive abrasive conditions, a new composite carbide based material has been applied (1982). Significant progress has been made, when high strength materials, and sealing compounds for

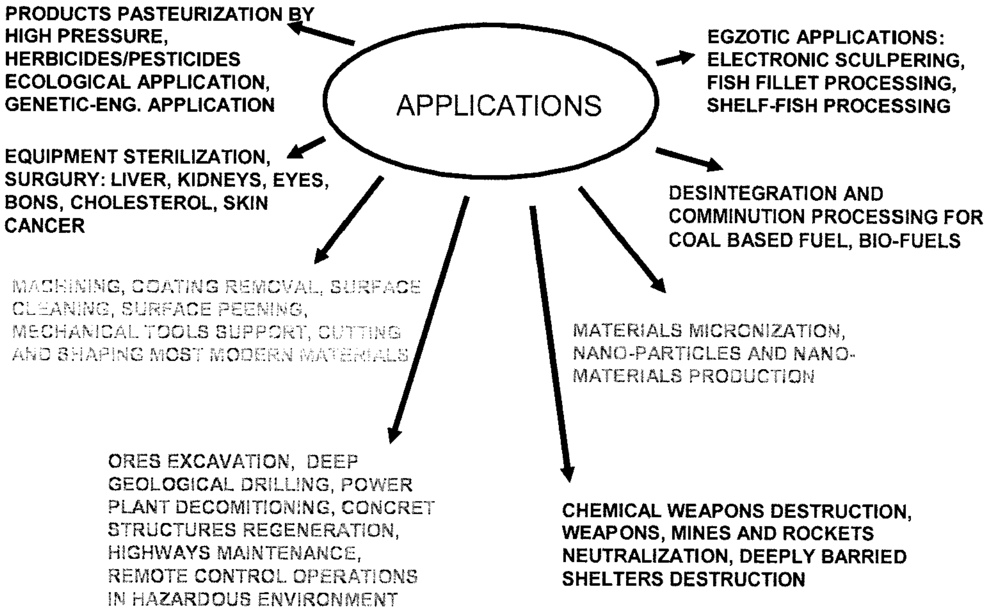


Fig. 1. Area of possible high pressure applications.

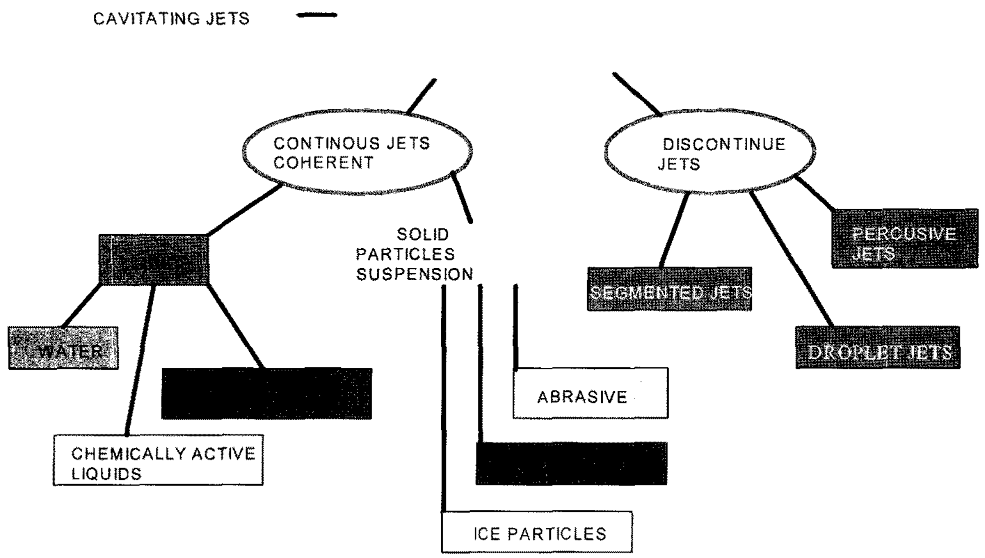


Fig. 2. Types of high pressure jets.

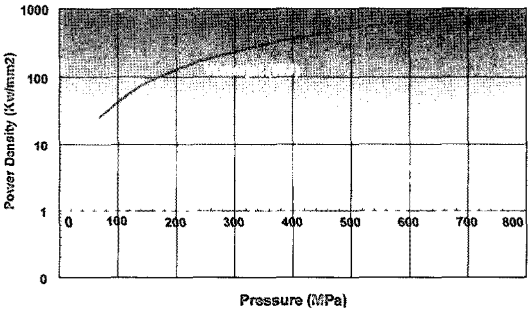


Fig. 3. Dependence of power density on liquid jet pressure.

high pressure were introduced to high pressure equipment. It made possible to apply pressure as high as 700 MPa so far (1995). The first international scientific conference devoted for high pressure water jet technology was organized in 1972 by BHRA. First USA conference was organized in 1980, and USWJTA was established.

Actually, there is no industry without high pressure liquid jet technology already applied, what is illustrated in Fig. 1. Such wide industrial applications are possible due to various forms of jets applied, what is shown in Fig. 2.

This relatively young technology is widely spread out and is recognized as a technology of 21st century. The newest part of this technology is a comminution technology by HJLJ invented just few years ago.

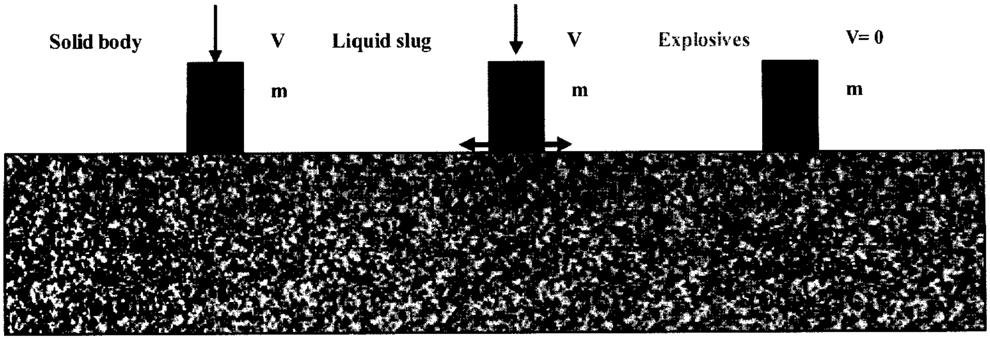
3. Ultra High Pressure Liquid Jet Technology

3.1. Basic principles

The basic tool of presented technology is ultra high pressure liquid jet, which generate necessary internal tensile pressure able to disintegrate a solid body or coarse particles into smaller ones, including nano sizes.

The dynamics of the liquid jet, generated under the pressure of 300-700 MPa, formed by the nozzle, could reach the speed of ca 4 M number, and generates significant power density shown in Fig. 3.

Its collision with the obstacle creates a number of phenomena which, in a very aggressive manner, disintegrate any matter into micron and nano-size particles. The phenomena include high speed collision, extremely high energy concentration at the collision interface, shattering and cleaving. The jet penetra-



*liquid hammer pressure , *differential pressure across the collision area , *lateral high speed flow, *micro-cracks formation , *cracks hydro-wedging , *shock propagation, *crack's tip acoustic speed propagation ,*aggressive cavitation

Fig. 4. Material response for different colliding slugs.

tion into cracks and micro-cracks, under high pressure, induces the propagation of cracks into the grain boundaries by hydro-wedging. The generation of new cracks can be supported by the water-hammer effect and the propagation of shock waves through the material. The radial outflow of the jet, with extremely high velocity, is assisted by a very aggressive cavitation, high turbulence flow, and high velocity collision/abrasion, which can cause the disintegration of any material in a short period of time. The jet, upon impact with the target, generates intense differential stagnation pressure, which forces the liquid into cracks and creates a hydro-mechanical action in these cracks, to form an increasingly dense network of new cracks. The induced cracks propagate with the speed of sound typical for the particular material.

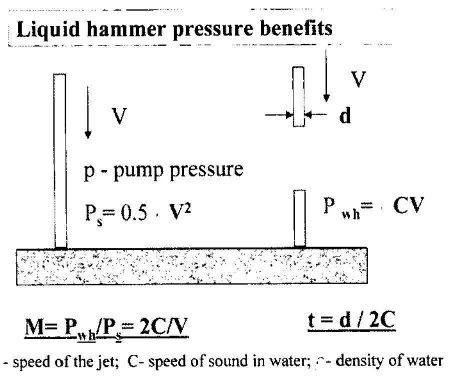
The superiority of the jet to disintegrate materials can be compared with the destruction by the same mass of solid body moving with the same velocity as a jet. The same mass of the explosives rested on the sample has been used for comparison in Fig. 4.

For the best possible implementation of all the above mentioned effects, special models of comminuting systems, based on linear and centrifugal reactor, have been designed, built and tested. Both systems are described in following chapters.

3.2. Hammer effect

The most up to date equipment can generate, at the collision interface, a power density close to 1000 kW/mm^2. This power is a function of the pressure before the nozzle which shapes the jet, jet velocity, and the jet diameter. To achieve a power concentration significantly above that point, a segmented jet must be applied instead of a continuous one. The benefits of the segmented jet over a continuous jet are explained in the Fig. 5.

It is a straight forward observation, that when

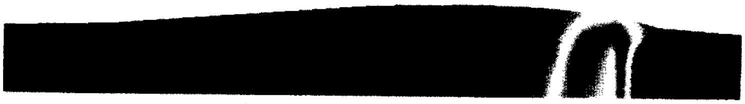


V - speed of the jet; C- speed of sound in water; ρ- density of water

p [MPa]:	34.5	103.5	138.0	
M =	11.6	6.7	5.8	For V = C ; M = 2

t [0.5mm] = 0.167 micro-seconds

Fig. 5. Liquid hammer pressure benefits.



(A) 79 µs after start of calculations

(B) 80 µs after start of calculations

(C) 81 µs after start of calculations

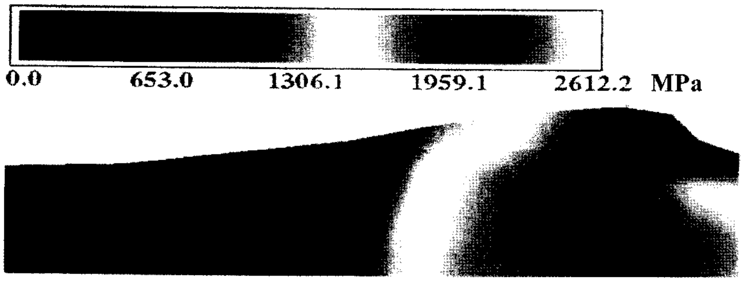


Fig. 6. Pressure distribution on the target at 81.2 ms for the discharge energy 20 kJ. Inlet pressure-34.5 MPa, flow - 49 lpm.

using segmented jets the pressure gain at the collision interface is many times higher than for a continuous jet. A good illustration of how high this pressure could become is a model of the liquid segment collision [1, 2] and pressure generated by the "liquid hammer" presented in Fig. 6.

It can be seen that, for this specific example, the selected pressure at the collision area is in the range of 2600 MPa. The results of 5000 MPa were generated in practice as well [4].

3.3. Conclusions

Summarizing, one can say, that liquid jet, upon impact of the target generates intense differential stagnation pressure which forces the liquid into cracks and creates a hydro-mechanical action in these cracks, to form an increasingly dense network of new cracks. Induced cracks are propagating, in particular materials, even with the speed of sound.

The following phenomena are generated by the liquid jet:

- Tremendous energy concentration and stress application where there are particles.
- High turbulence and intensive abrasion.
- Ultra-high frequency pressure pulsation.
- High speed collisions between jet and particles (800-1300 m/s) and between particles.
- High shearing energy.
- Aggressive cavitation.
- Water-hammer and shock wave effects.
- Hydro-wedging.

4. Linear Comminuting System

4.1. Concept and prototype of linear reactor

To exploit all the properties of a high energy jet, for the purpose of comminution, a unique design approach has been taken to maximize the energy flux in the mill chamber to create extremely high turbulence. The design concept of the reactor [3], presented in Fig. 7 and its prototype in Fig. 8, has a comminuting chamber where a high energy jet, gen-

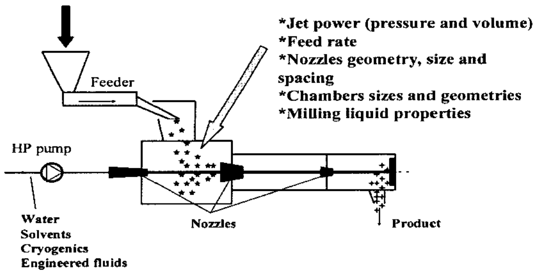


Fig. 7. Diagram and process parameters of linear comminuting system.

erated by the first nozzle, is aimed to a secondary nozzle, and then to the next nozzle placed in the second comminution chamber. The material is introduced into the comminuting chamber by the feeder.

All the particles in the comminuting chamber are exposed to highly turbulent movement and high velocity collisions with the jet at high frequency and collisions and abrasions with the chamber walls and between themselves.

Each particle is able to enter the second chamber only when its size is reduced enough to fit through the secondary nozzle. The design parameters and process parameters are very critical for the predicted product properties. After passing the second chamber the product is stopped on the collision plate and exits the reactor.

4.2. Test results

To demonstrate the application of the high energy jets for the comminution process, please find below the particle size analysis and scanning electron microscopy images of selected materials exhibiting particular characteristics after single and multiple passes through the reactor. These materials were processed at the pressure of 280 MPa. The list of tested materials and their comminution results is presented in Fig. 9.

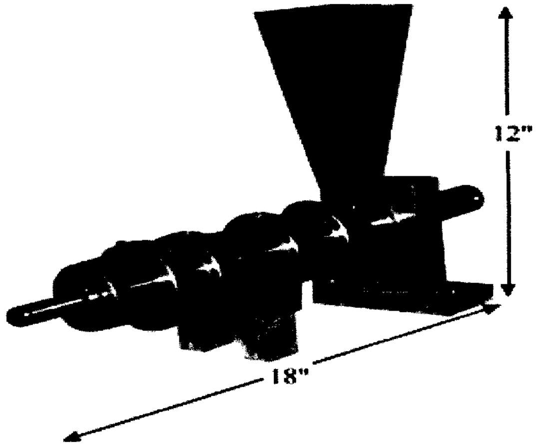


Fig. 8. Practical realization of the heart of linear comminuting system-linear reactor [3].

It can be seen that a variety of materials can be comminuted and that a single pass through the reactor creates a significant reduction in particle size.

To reach further reduction in particle size a multipass processing, shown in Fig. 10, should be applied. As a result of this system application, graphite nano

Typical single pass toll comminution results			
Material	**d_{50}**	**Material**	**d_{50}**
Silica	9 μm	Alumina	4 μm
Electronic Glass	59 μm	Nickel Metal	138 μm
Cordierite	13 μm	Silicon Carbide	25 μm
Wollastonite	28 μm	Titania Dioxide	4 μm
Silver Metal	5 μm	Graphite Natural and Synthetic	6 μm
Boron Carbide	150 μm	Dental Glass	3 μm
Silicon Metal	12 μm	Boron Nitride	6 μm
Anthracite	37 μm	Pyrophyllite	11 μm
Chromium	115 μm	Calcium Carbonate	7 μm
Barium Titanate	3 μm	Talc	7 μm
Zirconium Oxide	45 μm	Tin Oxide	N/A

* Incoming raw materials vary in size from 1cm d_{50} to 1mm d_{50}.

Fig. 9. Typical single pass toll comminution results.

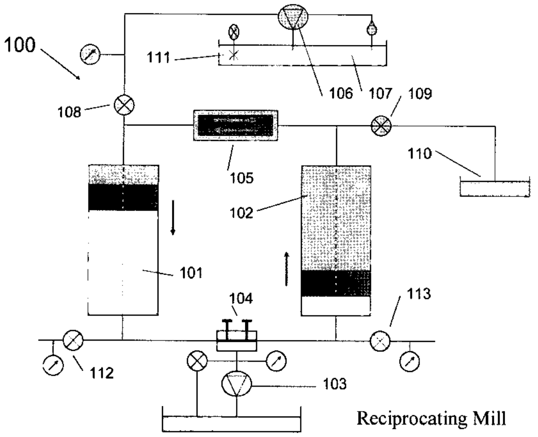


Fig. 10. Diagram of multi-pass, reciprocating system; main denotations: 101, 102-high pressure cylinders, 103-high pressure pump, 105-linear two ways reactor, 106-supply pump.

flacks have been produced. Synthetic graphite particles size distribution is shown in Fig. 11.

The thickness measurement of the graphite flakes is shown in Fig. 12.

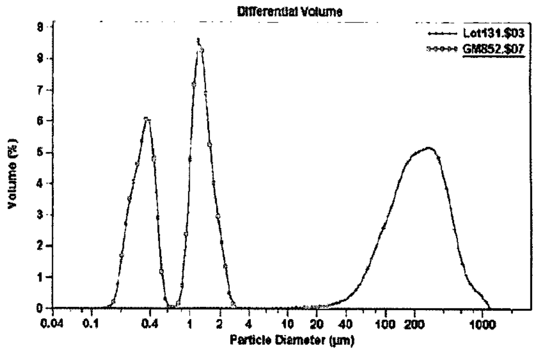
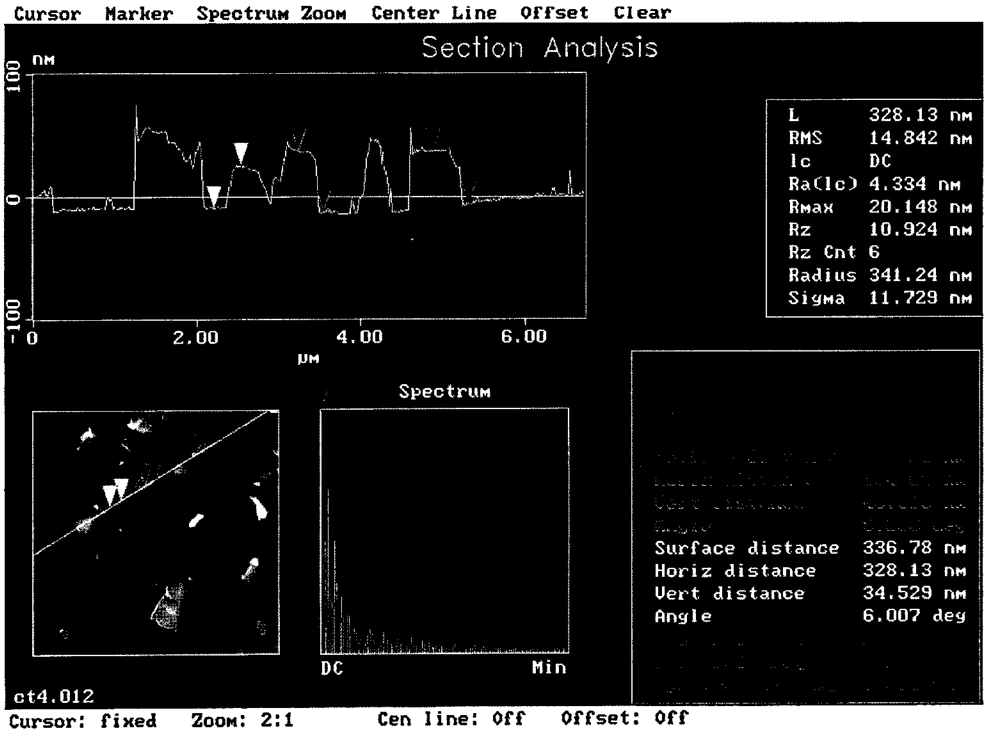


Fig. 11. Synthetic graphite particles size distribution.

The thickness range recorded was 30-50 nanometers [5].

Other interesting comminuting results were obtained in the case of acicular structures of certain silicates and ceramics (wollastonite). They maintain needle like structure and high aspect ratio when milled, what is shown in Fig. 13.

One can notice that average particle size 188 microns after one pass treatment has been reduced



L 328.13 nm
RMS 14.842 nm
Ic DC
Ra(Ic) 4.334 nm
Rmax 20.148 nm
Rz 10.924 nm
Rz Cnt 6
Radius 341.24 nm
Sigma 11.729 nm

Surface distance 336.78 nm
Horiz distance 328.13 nm
Vert distance 34.529 nm
Angle 6.007 deg

Cursor: fixed Zoom: 2:1 Cen line: Off Offset: Off

Fig. 12. Graphite flakes thickness measurement.

to 15 microns. It makes more than 10 times reduction.

5. Centrifugal Comminuting System

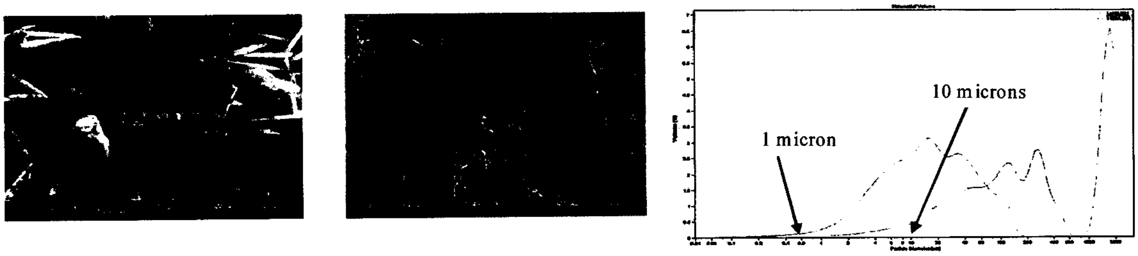
5.1. Concept and prototype of centrifugal reactor

Presented concept is based on centrifugal force. Dynamics of this process depends on disc's diameter and rotational speed. Expected colliding pressure on the collision ring surface is indicated in Fig. 13.

For the disc 4" diameter rotating with the speed 43,000 rpm calculated pressure is in a range of 100 MPa.

Production system, designated for deep micronization/nanonization could be build as shown in Fig. 14. This system allows performing this process in close circuit or open circuit. It can be run in dry or wet cycle, in inert environment, or in cryogenic conditions.

Prototype of this system is presented in Fig. 15.



FE-SEM micrograph at 250x magnification.

FE-SEM micrograph of typical product at 250x magnification. Note the very high aspect ratio needles created. Further comminution to produce lower aspect ratios can be achieved.

Raw Feedstock d_{50} = 188 μm, d_{100} = 2000 μm
Milled material d_{50} = 15 μm, d_{100} = 194 μm

Fig. 13. Comminution effect of ceramics with acicular structure.

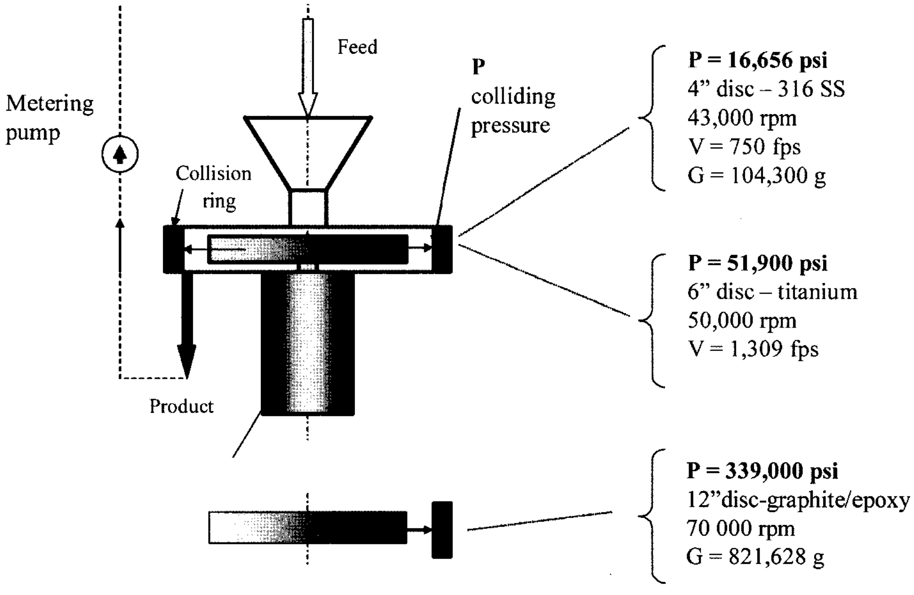


Fig. 14. Principles and parameters of centrifugal reactor.

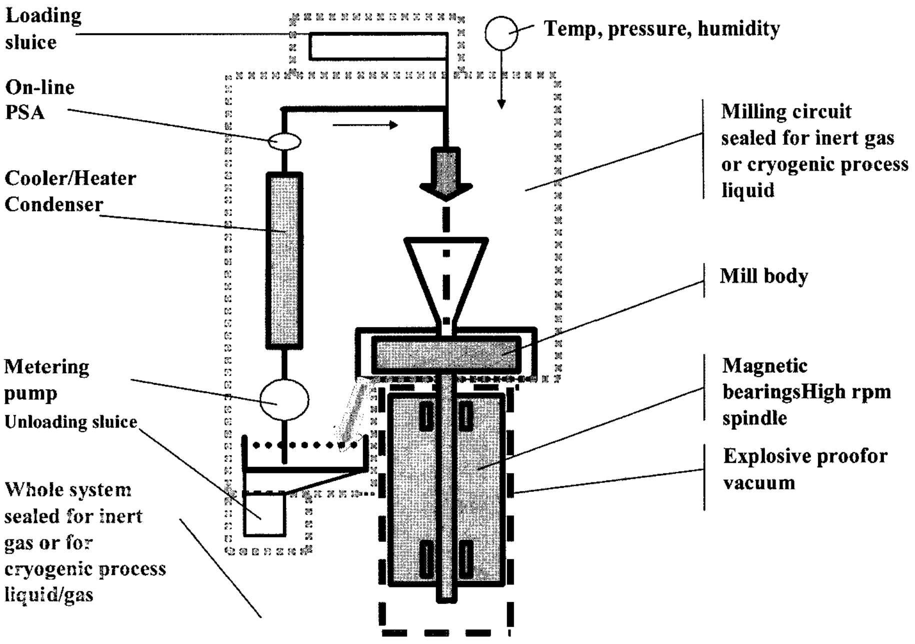


Fig. 15. Diagram of centrifugal comminuting system.

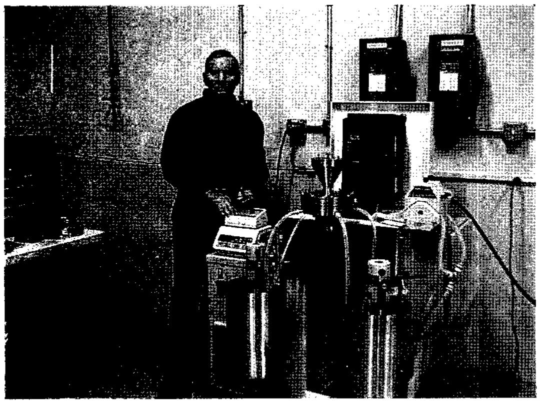


Fig. 16. Prototype of centrifugal comminuting system.

5.2. Test results

Coarse barium titanate particles, were very effectively comminuted by the centrifugal comminuting system. An effect of a single pass through the system is shown in Fig. 16.

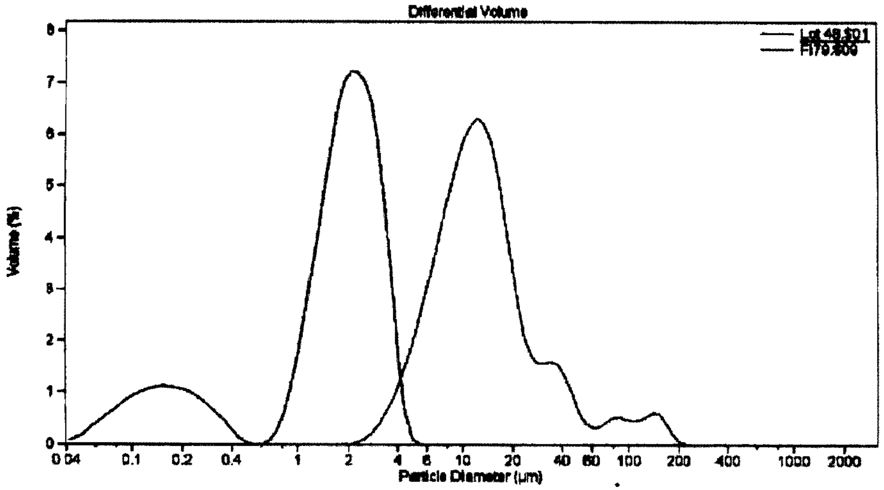
Silver particles produced by a conventional precipitation process were very effectively densified from tap density 1.8 to 6.89 g/cc. The particles before and after densification in centrifugal comminuting system are shown in Fig. 17.

6. Technical and Technological Benefits

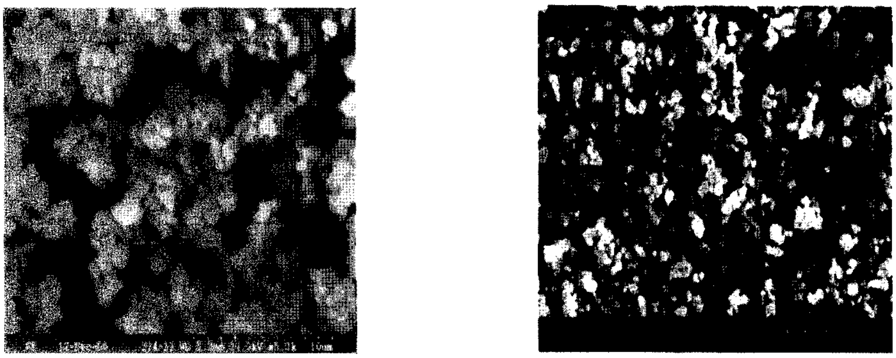
The designed and tested prototypes of reactors make it possible to easily adjust the comminution parameters for a particular material and tailor the process to expected product characteristics. The process can be adjusted by changing the energy of the jet (pressure, volume), feed rate, nozzle geometry (size and spacing), chamber size and geometry, and the liquid characteristics of the process.

During R&D the following benefits of high energy liquid jet comminution were observed:

- Depending on the feed material and process parameters the output of a single mill can be as high as 1000 kg/h.
- The particle size reduction observed was 10 to 1000 fold.
- A needle type or layered material can be comminuted with a very high aspect ratio not achievable using a conventional milling processes.
- The ability of the jet to create hydro-wedging and attack the natural crystal borders, material



Single Pass Barium Titanate



Raw Barium Titanate 5k

Milled Barium Titanate 3k

Fig. 17. Barium titanate before and after milling (single pass).

flaws, discontinuities, and micro-cracks during the comminution process results in unprecedented particle rheology.

- The process generates extremely low contamination.
- The liquid used for the process could be selected from water, solvent, cryogenic liquid and in some instances specially engineered fluid.
- The process can be conducted by feeding multiple components at the same time allowing for chemical reactions during the process and mixing fed components in an unprecedented way.
- Dry particles or liquid suspensions can be fed into the chamber.
- The system can be run under pressure up to 700 MPa.
- The system is highly reliable.

The way this reactors are designed and the flexibility in using it makes for an excellent starting point for further milestones in creating liquid metals, nano-dispersions, metallic nano-suspensions, material synthesis, magnetic micro and nano-particles, amorphous materials and pharmaceutical nano-formulations.

7. Summary

- The current state of the art in comminution tech-

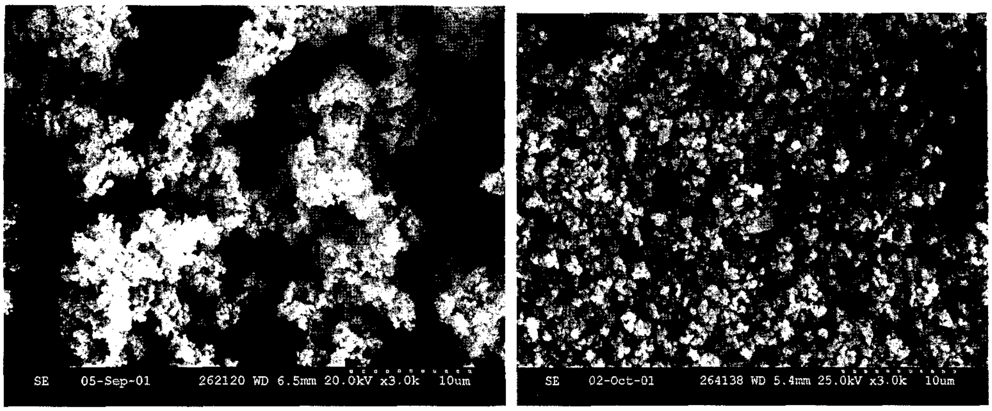


Fig. 18. Silver powder before and after densification.

nology has many shortcomings, what stimulate for explore new solutions.

- The process and equipment introduced in this paper indicate that presented new material disintegration physics can be exploited to make the process more efficient with many technological benefits.
- Exploitation of high pressure/high speed liquid flow creates environment where many physical phenomena takes place simultaneously. It makes macronization/nanonization, densification and homogenization very effective and very potential industrially; particularly that achievable output of a single mill can be as high as 1000 kg/h.
- Very essential feature of disintegrated particles is their rheology, favorable for many applications. This unprecedented particle rheology owes to the liquid jet action, which coarse particle disintegration propagates mostly along its natural crystal borders.
- Additional favorable feature of presented technology is fact, that the process generates extremely low contaminations.
- The flexibility of the system and achieved results thus far indicate a good opportunity for further improvement and adaptations of ultra-high pressure liquid jet technology for various industrial applications.
- The results achieved so far are very encouraging and the prospect of industrial application makes the authors believe that the experts attending ISNNM 2008 will embrace our observations.

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