Review Paper on Perovskite Prepared by Reactive Grinding

Dhaval Tank, Femina Patel and Sanjay Patel

Abstract-- **The main objectives of catalytic control of air pollution is to purify automobile exhaust gases which can cause serious environmental problems such as photochemical smog, acid rain, ground level ozone and respiratory diseases. Perovskite oxides is promising alternatives to supported noble metals for exhaust gas depollution because of their low cost, thermal stability at rather high temperatures, great versatility and excellent redox properties.**

The major traditional drawback of perovskites is the low specific surface area (usually several m^2/g) due to their preparation which involves high temperature (often as high as 800 ^0C) to ensure the formation of the crystalline phase. This suppresses their activity and to some degree limits their application. A new preparation method called reactive grinding is developed for the synthesis of perovskites at room temperature via high-energy ball milling which results in a relatively high surface area when grinding additives are used.

This review paper discuses automotive exhaust emissions and its impact, automotive exhaust emission control by platinum (noble) group metal based catalyst in catalytic converter, reactive grinding via high-energy ball milling, types of high energy ball mill, process variables in milling, synthesis of perovskite by reactive grinding.

Key words: Automotive emission; Catalytic converter; High energy ball milling; Perovskite; Reactive grinding

I. INTRODUCTION

Air pollution generated from mobile sources is a problem of general interest. In the last 60 years the world vehicle fleet has increased from about 40 million vehicles to over 700 million; this figure is projected to increase to 920 million by the year 2010 [1]. Engine exhausts consist of a complex mixture and its composition depending on a variety of factors such as: type of engine (two or four stroke, spark or compression (diesel) ignited), driving conditions. (e.g. urban or extra-urban), vehicle speed (acceleration/deceleration) etc. [2]. Due to incomplete combustion in the engine, there are a number of incomplete combustion products. At high temperature during combustion in the cylinder N_2 and O_2 react to establish with NO, this equilibrium is frozen as the hot gases are cooled and ejected into the exhaust manifold. The combination of NO and NO_2 is referred to as NO_x and more than a 1000 ppm can be present in exhaust of a gasoline engine.

The main pollutants in exhaust gases from vehicle engines include carbon dioxide, carbon monoxide, unburned hydrocarbon (Hydrocarbon mixture contains a large variety of hydrocarbons out of which mainly present hydrocarbons are ethylene, acetylene, propane and propene), nitrogen oxides (NO_x), sulphur dioxide and particulates matter can cause serious environmental problems such as photochemical smog, acid rain, ground level ozone and respiratory diseases [3]. Thus, the use of catalysts for purifying exhaust gases is absolutely necessary and indispensable in every vehicle. The technology to convert simultaneously all these pollutants (CO, HC, and NO_x) into innocuous materials are referred to as three way catalysis or three way catalytic converter (TWCs). The important role of automotive catalysts in catalytic converter contain precious metals palladium (Pd), Platinum (Pt) and rhodium (Rh) is widely recognized for the conversion of three pollutant emissions such as carbon dioxide (CO) into CO_2, nitrogen oxides (NO_x) to nitrogen and unburned hydrocarbons (HC) into CO_2 and water in engine exhaust gases (Car's tail pipe).

Catalysts are composed of several components including noble metals (Pt, Pd and Rd) as active site, alumina-based supports with a high surface area and metal oxides as promoter material. The catalytic converters are, in fact, reactors that consist of monolithic honeycombs skeleton made of ceramic or metallic materials. Monolith is first coated with high surface area oxide like γ-Al_2O_3 and the process is called wash coating. After wash coating, the three way catalyst [Pt, Pd and other platinum group (PGM)] usually called active phase is coated over monolith [4]-[6].

However, due to the rising cost of PGM, sintering at high temperature and volatilization, many researchers have been searching for alternative materials as the active catalytic phase. One of the promising active material for the environmental applications is the perovskite group of materials ($ABO_{3:}$ A: rare earths, B: transition metals of the first row), where A and B are cations of different sizes. ABO_3 perovskite oxides have been propose as promising three way catalysts for the removal of exhaust gases since 1970's because of their low cost, thermal and mechanical stability at relatively high temperature great diversity and excellent redox properties.

The catalytic properties of perovskite-type oxides basically depend on the nature of A and B ions and on their valence state. The A site ions are catalytically inactive. The nature of these ions however also influences the stability of the perovskite phase. Catalytic activity is generally determined by the B cation. Several methods are used to synthesis perovskites such as co-precipitation, sol-gel, citrate complexation, micro-emulsion etc. Calcination at high temperatures is necessary for almost all of these methods. Such treatments often result in a sharp decrease of the surface area of the catalyst thus yielding low catalytic activity per unit mass. For example, Co-based perovskite catalysts prepared by the conventional citrate complexation method have a surface area of only 4–7 m^2/g after calcination at 600 ^0C for 6 h [7]. The specific surface area observed on perovskites prepared by these methods rarely exceeds 25 m^2/g. A new preparation method for perovskite can allow to avoid the thermal treatment and the crystallize to proceed at nearly ambient temperature. This technique uses high energy ball milling (reactive grinding) resulting in relatively high surface area. The structures prepared by reactive grinding present nanometric-size particles and large specific surface areas which can exceed 100 m^2/g [8], [9]. Using various grinding additives, high surface (measured after calcinations at 473 K) perovskites such as $LaCoO_3$ (>100m^2/g), $LaGaO_3$ (98.6 m^2/g), $LaCo_xIn_{1-x}O_3$ (>110 m^2/g) or $SrCoO_3$ (150 m^2/g) were consistently prepared [10].

This review paper discuses automotive exhaust emissions and its impact, automotive exhaust emission control by platinum (noble) group metal based catalyst in catalytic converter, reactive grinding via high-energy ball milling, types of high energy ball mill, process variables in milling, synthesis of perovskite by reactive grinding.

II. REACTIVE GRINDING

Mechanochemical is also known as reactive griniding. Mechanochemical processing (MCP) or mechanochemical synthesis is the term applied to powder processing in which chemical reactions and phase transformations take place during milling due to the application of mechanical energy [11]-[14]. An important feature of the process is that plastic deformation and chemical processes occur almost simultaneously. The process of mechanical alloying (MA) starts with mixing of the powders in the desired proportion and loading of the powder mix into the mill along with the grinding medium (generally carbon steel, tungsten carbide, stainless steel balls) in which powder particles are subjected to repeated cold welding, fracturing and rewelding. Sometimes a process control agent (PCA) is added to prevent or minimize excessive cold welding of powder particles among themselves and/or to the milling container and the grinding medium. This mix (with or without the PCA) is then milled for the required length of time until a steady state is reached. Reactive grinding can be done easily under solvent-free conditions and rapidly produces large amounts of well-mixed nanocomposites [15]. Metal powder mixtures are milled with a liquid medium (here the liquid only facilitates milling but does not take part in alloying with the powder) and this is referred to as wet grinding if no liquid is involved the process is called dry grinding [16], [17].

Types of High energy ball mill

Different types of high-energy milling equipment are used to produce mechanically alloyed/milled powders. They differ in their design, capacity, efficiency of milling and additional arrangements for cooling, heating and so forth. The following sections describe some of the more common mills currently in use for Mechanical alloying and Mechanical Milling [18].

(1) Spex Shaker Mills

Shaker mills, such as SPEX mills which mill about 10–20 g of the powder at a time are most commonly used for laboratory investigations [19]. The common version of the mill has one vial containing the powder sample and grinding balls, secured in the clamp and swung energetically back and forth several thousand times a minute. Because of the amplitude (about 5 cm) and speed (about 1200 rpm) of the clamp motion, the ball velocities are high (on the order of 5 m/s) and consequently the force of the ball's impact is unusually great. Therefore, these mills can be considered as high-energy ball mill. SPEX mills have certain disadvantages. First, the balls may roll around the end of the vial rather than hitting it; this decreases the intensity of milling. Second, the powder may collect in the eyes of the ''8'' and remain unprocessed. Last, the round-ended vial is rather heavy; the flat-ended vial is 30% lighter and impacts at the ends of the vial dominate the milling action. However, some powder may collect at the edges and remain unprocessed [20].

(2) Planetary Ball Mills

Planetary ball mill in which a few hundred grams of the powder can be milled at the same time. The planetary ball mill owes its name to the planet-like movement of its vials. These are arranged on a rotating support disk and a special drive mechanism causes them to rotate around their own axes. The centrifugal force produced by the vials rotating around their own axes and that produced by the rotating support disk both act on the vial contents consisting of the material to be ground and the grinding balls. The superimposition of the centrifugal forces produces grinding ball movements with a high pulverization energy. The centrifugal forces acting on the grinding jar wall initially carry the grinding balls in the direction in which the grinding jar is rotating. Differences occur between the speed of the grinding jar wall and the balls; this results in strong frictional forces acting on the sample. As the rotational movement increases, Coriolis forces act on the balls to displace them from the grinding jar walls. The balls fly through the grinding jar interior and impact against the sample on the opposite grinding jar wall. This releases considerable dynamic impact energy. The combination of the frictional forces and impact forces causes the high degree of size reduction of planetary ball mills.

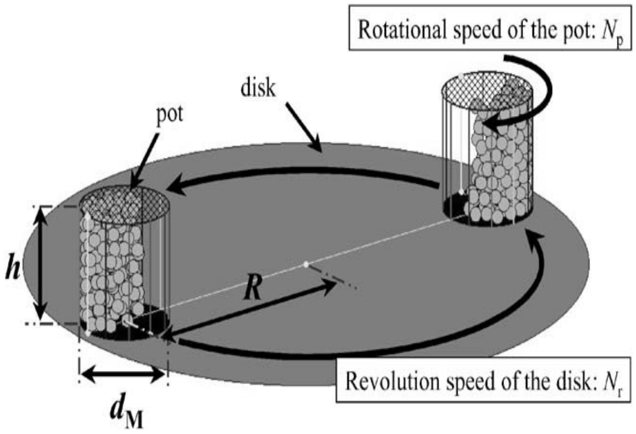

Fig. 1: Planetary ball-mill [21]

(3) Attritor Mills

Attritors also known as stirred ball mills are the mills in which large quantities of powder (from a few pounds to about 100 lb) can be milled at a time. An attritor (a ball mill capable of generating higher energies) consists of a vertical drum containing a series of impellers. A powerful motor rotates the impellers which in turn agitate the steel balls in the drum. Set progressively at right angles to each other, the impellers energize the ball charge. The dry particles are subjected to various forces such as impact, rotation, tumbling and shear. This causes powder size reduction. Because of collisions between balls, between balls and container wall and between balls, agitator shaft and impellers. Therefore, micrometer-range fine powders can be easily produced.

(4) Commercial Mills

Commercial mills for MA are much larger in size than the mills described above and can process several hundred pounds of powder at a time. MA for commercial production is carried out in ball mills of up to about 3000 lb (1250 kg) capacity.
The milling time decreases with an increase in the energy of the mill. It has been reported that 20 min of milling in a SPEX mill is equivalent to 20 h of milling in a low energy mill. As a rule of thumb, it can be estimated that a process that takes only a few minutes in the SPEX mill may take hours in an attritor and a few days in a commercial mill, even though the details can differ depending on the efficiency of the different mills [17].

III. PROCESS VARIABLES IN MILLING

Mechanical alloying (MA) is a complex process involving optimization of a number of process variables to achieve the desired product phase, microstructure, and/or properties [22]. However, we will not consider the nature and composition of the powder mix as a variable here. For a given composition of the powder, some of the important variables that have an important effect on the final constitution of the milled powder are as Type of mill, Milling container, Milling energy/speed, Milling time, Type, size, and size distribution of grinding medium, Ball-to-powd er weight ratio, Extent of vial filling, Milling atmosphere, Process control agent, Temperature of milling. These process variables are not completely independent. For example, the optimal milling time depends on the type of mill, size of the grinding medium, temperature of milling, ball-to-powder ratio (BPR), etc. Further, more energy could be imparted to the milled powder by increasing the BPR or by milling the powder for a longer time. Similarly, it could be shown that some of the other parameters are also interdependent.

(1) Type of Mill

The mills differ in their capacity, speed of operation and capacity to control the operation by varying the temperature of milling and the extent of minimizing contamination of the milled powders. Depending on the type of powder, the quantity of powder to be milled and the final constitution required, a suitable mill can be chosen.

(2) Milling Container

The material used for the milling container (grinding vessel, vial, jar and bowl are some of the other terms used) is important because due to impact of the grinding medium on the inner walls of the container some material will be dislodged and be incorporated into the powder. This can contaminate the powder and/or alter the chemistry of the milled powder [23].

(3) Milling Energy/Speed

It is easy to realize that the faster the mill rotates the higher will be the energy input into the powder due to the kinetic energy supplied to the powder is higher at higher relative velocities of the grinding medium. However, depending on the design of the mill there are certain limitations to the maximal speed that could be employed. For example, in a conventional ball mill increasing the speed of rotation will increase the speed with which the balls move. .Above a critical speed, the balls are pinned to the inner walls of the vial and do not fall down to exert any impact force. Therefore, the maximal speed should be just below this critical value so that the balls fall down from the maximal height to produce the maximal collision energy.

Limitation to the maximal speed is that at high speeds (or intensity of milling) the temperature of the vial may reach a high value. This may be advantageous in some cases where diffusion is required to promote homogenization and/or alloying in the powders. However, in some cases this increase in temperature may be a disadvantage because the increased temperature accelerates the transformation processes and results in the decomposition of supersaturated solid solutions or other metastable phases formed during milling [23].

(4) Milling Time

Normally the time is chosen to achieve a steady state between fracturing and cold welding of powder particles to facilitate alloying. The times required vary depending on the type of mill used, mill settings, intensity of milling, BPR and temperature of milling. The necessary times have to be decided for each combination of the above parameters and for the particular powder system under consideration [24].As a general rule, it may be appreciated that the times taken to achieve the steady-state conditions are short for high-energy mills and longer for low-energy mills. Again, the times are shorter for high BPR values and longer for low BPR values.

(5) Grinding Medium

Different grinding media like hardened steel, tool steel, hardened chromium steel, tempered steel, stainless steel, WC-Co and bearing steel are used as a grinding media. The density of the grinding medium should be high enough that the balls create enough impact force on the powder to affect alloying. It is desirable, when possible to have the grinding vessel and the grinding medium made of the same material as the powder being milled to avoid cross contamination of the milled powder [23].

(6) Ball-To-Powder Weight Ratio

The ratio of the weight of the balls to the powder (BPR), sometimes referred to as charge ratio (CR). Very high values of BPR are uncommon and values such as 1000:1 or 220:1 [25] are used only in special cases to achieve certain desired features or to achieve the effects faster. Even though a ratio of 10:1 is most commonly used while milling the powder in a small capacity. High-energy mill such as a SPEX mill, BPR values ranging from 4:1 to 30:1 have been generally used. The higher the BPR, the faster is the MA process. However, this faster processing also can introduce high contamination levels into the powder and this should be avoided or at least minimized.

(7) Extent of Filling the Vial

It is necessary that there be enough space for the balls and the powder particles to move around freely in the milling container. If vial is full with balls then grinding of materials will be less because there is not movement of balls. If the quantity of the balls and the powder is very small then the production rate is very low and vice-versa. Thus, care must be taken not to overfill the vial; generally about 50% or a little more of the vial space is left empty [26].

(8) Milling Atmosphere

The major effect of the milling atmosphere is on the nature and extent of contamination of the powder. Nitrogen or ammonia atmosphere has been used to produce nitrides [27], [28]. Hydrogen atmosphere was used to produce hydrides [29]. The presence of air in the vial has been shown to produce oxides and nitrides in the powder especially if the powders are reactive in nature. Thus, care must be taken to use an inert atmosphere during milling.

(9) Process Control Agent

A process control agent (PCA) (also referred to as lubricant or surfactant) is added to the powder mixture during milling to reduce the effect of excessive cold welding. PCAs can be solid, liquid, or gaseous. They are mostly but not necessarily organic compounds which act as surface-active agents. They adsorb on the surface of the powder particles and minimize cold welding among powder particles thereby inhibiting agglomeration. The surface-active agents adsorbed on particle surfaces interfere with cold welding and lower the surface tension of the solid material. A wide range of PCAs has been used in practice at a level of about 1–5 wt% of the total powder charge. The most important PCAs include stearic acid, hexane, methanol, and ethanol [30].

(10) Temperature of Milling

The temperature of milling is another important variable in deciding the constitution of the milled powder. Since diffusion processes are involved in the formation of alloy phases irrespective of whether the final product phase is a solid solution, intermetallic, nanostructure or an amorphous phase, it is expected that the temperature of milling will have a significant effect in any alloy system [31].

IV. SYNTHESIS OF PEROVSKITE BY REACTIVE GRINDING

Perovskite type materials $LaCoO_3$ was prepared from their component oxides by mechano-synthesis by reactive ball grinding method. When grinding additives are added ,the perovskites generated by this method has a unprecedently high surface area (>100m^2/g) .The perovskite surface shows a large concentration of surface OHs due to low grinding temperature which upon calcination leads to reformation of the material lattice. The presence of oxygen during calcinations initiates a competitive process ,which stabilizes the sites with an excess of electronic charge ,yielding reduced Co sites upon oxygen desorption (Co^{2+}).Reactive ball grinding method also allows preparation at rather low temperature of crystalline oxide phases normally produced at very high temperatures.

As starting compounds, lanthanum oxide (La_2O_3) (99.99 % pure) and Cobalt oxide Co_3O_4 (97.49 %) of the analytic grade were used. $LaCoO_3$ sample was prepared from simple oxides by using preliminary mechanical treatment (MCA) of the stochiometric of simple oxides with steel balls in the high energy ball mill i.e. planetary mills.

The La_2O_3 was first calcined at 873 K for 24 hours in order to transform any lanthanum hydroxide to lanthanum oxide. Thus 15 gm of prepurified lanthanum oxide and 5 gm of cobalt oxide were mixed (La/Co atomic ratio equal to 1) and introduced in a grinding jar of volume 250 cm^3 with 12 balls of 20 mm size and 10 balls of 10 mm size. The jar and the balls are made with stainless steel material. The jar was closed with a thick cover and sealed with O-ring.

Table I
BALL MILL OPERATING CONDITIONS

Operating conditions	
Material of jar and ball	Stainless steel
Speed ratio (Sun wheel and jar speed ratio)	1:-2
jar speed (rpm)	300
Sunwheel speed(rpm)	150
Ball diameter (cm)	10 mm (09) 14 mm (11) 19 mm (10)
Mass of powder in jar in (gm)	15
Grinding Jar dimension: $d_i = 67.5$ mm $d_o = 78$ mm h = 71.5 mm Jar volume (cm^3) = $\frac{\Pi}{4} d_i^{\,2} h$ $= \frac{\Pi}{4} 67.5^2 \times 71.5$ = 255.8 cm^3	≅ 250

The mixture was intensively milled for 4.5 hrs in planetary ball mill under the following conditions: air atmosphere, stainless steel jar of 250 cm^3 volume, stainless steel balls of a diameter 10 mm (09), 14 mm (11) and 19 mm (10) mass of the powder 15 gm, ball to powder weight ratio of 29:1, basic disc rotation speed (sun wheel) 150 rpm, grinding jar rotation speed 300 rpm.

The balls and the powder were put inside the grinding jar of planetary ball mill. On another side of the grinding jar balls of the weight equal to the weight of the material and powder in the first grinding jar were added so that the weight is balanced. Although milling proceeds at room temperature, the numerous ball shocks within the jar slightly increases its temperature. Thus the container was fan cooled and its wall temperature is kept below 313 K .The milling atmosphere in the jar could be controlled by replacing the seal by a filter paper ring in order to let some air seep into the jar (oxidizing atmosphere). In the sealed jar the oxygen in the trapped air is rapidly consumed. The Revolution per minute (rpm) of the sun wheel was kept at 150 and that of jar at 300.The speed of sun wheel to jar should be maintained in ratio of 1:-2. The milling was carried out for 4.5 hours.

Fig. 2: Grinding Balls and High Energy Ball Mill (Planetary ball mill)

V. Characterization

Table II
PROPERTIES OF $LaCoO_3$ AFTER CALCINATION AT 600 ^{0}C FOR 5 Hr

Sample	**Calcination T (^{0}C)**	**XRD**	**Specific Surface Area (m^2/g)**	**Pore vol. Cm^3/gm**	**Pore Dia. nm**
$LaCoO_3$ (15 hr) by reactive grinding	600	P+O	7.8624	0.0268	19-22
$LaCoO_3$ By Sol gel		P	5.222	0.0358	26-39

P : $LaCoO_3$, O: La_2O_3, $CoCo_2O_4$

VI. Conclusion

Perovskite oxides promising alternatives to supported noble metals have attracted much attention for exhaust gas depollution because of their low cost, thermal stability at rather high temperatures, great versatility and excellent redox properties. A new preparation method for perovskite can allow to avoid the thermal treatment and the crystallize to proceed at nearly ambient temperature. This technique uses high energy ball milling (reactive grinding) resulting in relatively high surface area and also the synthesis is performed in a closed environment without generating any waste. Reactive grinding can be done easily under solvent-free conditions and rapidly produces large amounts of well-mixed nanocomposites that overcome the limitation of peovskite (low surface area) and make it commercialize for auto exhaust emission.

VII. References

[1] J. Kaspar, P. Fornasiero, N. Hickey, "Automotive catalytic converters: current status and some perspectives", *Catalysis Today,* vol. 77, pp. 419–449, 2003.

[2] R. Heck, R. Farrauto, "Automobile exhaust catalysts", *Applied Catalysis A:* General, vol. 221, pp. 443–457, 2001.

[3] M. Twigg, "Roles of catalytic oxidation in control of vehicle exhaust emissions", *Catalysis Today,* vol. 117, pp. 407–418, 2006.

[4] A. Mouza, C. Peolides, S. Paras, "Utilization of used auto-catalytic converters in small countries: the greek paradigm",

Resources, Conservation and Recycling, vol. 15, pp. 95-110, 1995.

[5] J. Hoebink, R. van Gemert, J. van den Tillaart, G. Marin, "Competing reactions in three-way catalytic converters: modeling of the NO_x conversion maximum in the light-off curves under net oxidizing conditions", *Chemical Engineering Science*, vol. 55, pp. 1573-1581, 2000.

[6] B. Levasseur, S. Kaliaguine, "Methanol oxidation on $LaBO_3$ (B = Co, Mn, Fe) perovskite-type catalysts prepared by reactive grinding", *Applied Catalysis A: General*, vol. 343, pp. 29–38, 2008.

[7] Y. Chang, J. McCarty, "Novel oxygen storage components for advanced catalysts for emission control in natural gas fueled vehicles", *Catalysis Today,* vol. 30, pp. 163-170, 1996.

[8] B. Seyfia, M. Baghalha, H. Kazemian, "Modified $LaCoO_3$ nano-perovskite catalysts for the environmental application of automotive CO oxidation", *Chemical Engineering Journal*, vol. 148, pp. 306–311, 2009.

[9] P. Avila, M. Montes, E. Miro, "Monolithic reactors for environmental applications A review on preparation technologies", *Chemical Engineering Journal*, vol. 109, pp. 11–36, 2005.

[10] V. Szabo, M. Bassir, A. Van Neste, S. Kaliaguine, "Perovskite-type oxides synthesized by reactive grinding Part II: Catalytic properties of $LaCo_{(1-x)}Fe_xO_3$ in VOC oxidation", *Applied Catalysis B: Environmental*, vol. 37, pp. 175–180, 2002.

[11] S. Kaliaguine, A. Van Neste, V. Szabo, J. Gallot, M. Bassir, R. Muzychuk, "Perovskite-type oxides synthesized by reactive grinding Part I. Preparation and characterization", *Applied Catalysis A: General*, vol. 209, pp. 345–358, 2001.

[12] R. Zhang, A. Villanueva, H. Alamdari, S. Kaliaguine, "Catalytic reduction of NO by propene over $LaCo_{1-x}Cu_xO_3$ perovskites synthesized by reactive grinding", *Applied Catalysis B: Environmental*, vol. 64, pp. 220–233, 2006.

[13] R. Zhang, H. Alamdari, S Kaliaguine, "Fe-based perovskites substituted by copper and palladium for NO + CO reaction", *Journal of Catalysis*, vol. 242, pp. 241–253, 2006.

[14] V. Szabo, M. Bassir, A. Van Neste, S. Kaliaguine "Perovskite-type oxides synthesized by reactive grinding Part IV. Catalytic properties of $LaCo_{1-x}FexO_3$ in methane oxidation", Applied *Catalysis B:* Environmental, vol. 43, pp. 81–92, 2003.

[15] L. Wang, Y. Liu, M. Chen, Y. Cao, H,Yong, W. Gui-Sheng , W. Dai, K. Fan, "Production of hydrogen by steam reforming of methanol over Cu/ZnO catalysts prepared via a practical soft reactive grinding route based on dry oxalate-precursor synthesis", *Journal of Catalysis*, vol. 246, pp. 193–204, 2007.

[16] A. Bellosi, F. Monteverde, S. Botti, S. Martelli, "Development and Characterization of Nanophase Si_3N_4-Based Ceramics", *Material science forum*, vol. 235-238, pp. 255-260, 1997.

[17] G. Nicoara, D. Fratiloiu, M. Nogues, J.L. Dormann, F. Vasiliu, "Ni-Zn Ferrite Nanoparticles Prepared by Ball Milling", *Material science forum*, vol. 235-238, pp. 145-150, 1997.

[18] P. Duwez, "Structure and Properties of Glassy Metals", Annual Review of Materials Science, *Material Research*, Vol. 6, pp. 83-117.

[19] C. Suryanaryan, Mechanical Alloying and Milling, Marcel Dekker New York, Chapter 4, pp. 35-57.

[20] D. Gavrilov, O. Vinogradov, W. Shaw, "Simulation of grinding in a shaker ball mill", *Powder Technology,* vol. 101, pp. 63–72, 1999.

[21] H. Mio, J. Kano, F. Saito, "Scale-up method of planetary ball mill", *Chemical Engineering Science*, vol. 59, pp. 5909 – 5916, 2004.

[22] S. Grugeon-Dewaele, S. Laruelle, F. Joliveau-Vallat, L. Torcheux, A. Delahaye-Vidal, "Synthesis and electrochemical preformances of tribasic and tetra basic lead sulfates prepared by reactive grinding", *Journal of Power Sources*, vol. 72, pp. 126–131, 1998.

[23] K. Venkataraman, K. Narayan, "Energetics of collision between grinding media in ball mills and mechanochemical effects", *power technology*, vol. 96, pp. 190-201, 1998.

[24] S. Tadier, N. Bolay, C. Rey, C. Combes, "Co-grinding significance for calcium carbonate–calcium phosphate mixed cement. Part I: Effect of particle size and mixing on solid phase reactivity", *Acta Biomaterialia*, 2010.

[25] K. Miklos, D. Beke, "Phase Transitions in Cu-Sb Systems Induced by Ball Milling", Material Science Forum, vol. 225–227, pp. 465–470, 1996.

[26] Woo Sik Choi et al., "Amorphous ultrafine particle preparation for improvement of bioavailability of insoluble drugs: grinding characteristics of fine grinding mills", *International Journal of Mineral Processcing*, Vol. 74, pp. 165–172, 2004.

[27] M. Miki, T. Yamasaki, Y. Ogino, "Preparation of Nanocrystalline NbN and (Nb, Al)N Powders by Mechanical Alloying under Nitrogen Atmosphere", *Material Transactions Japan Institute of Metals,* vol. 33, pp. 839–844, 1992.

[28] A. Calka, J. Williams, "Synthesis of nitrides by mechanical alloying", *Material Science* Forum, vol. 88–90, pp. 787–794, 1992.

[29] Y. Chen, J. Williams, "Hydriding Reactions Induced by Ball Milling", *Material Science Forum*, vol. 225–227, pp. 881–888, 1996.

[30] J. Chitralekha, K. Raviprasad, E. Gopal, K. Chattopadhyay, "Formation of metastable phase in mechanicaaly alloyed tellurium-rich Ag-Te alloys", *Journal of Material Research*, vol. 10, pp. 1897–1904, 1995.

[31] Z. Fu, W. Johnson, "Nanophase Zr-Al solid solutions by mechanical alloying at elevated temperatures", *Nanostructured Material*, vol. 3, pp. 175–180, 1993.