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RAPID SYNTHESIS OF FUNCTIONAL MATERIALS BY ELECTRIC DISCHARGE ASSISTED MECHANICAL MILLING

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Abstract. Many functional materials are traditionally synthesized by slow reaction processes that are energy and time consuming. In the present world there is strong demand on development of modern materials and materials processing methods that could offer rapid reaction rates, energy efficiency and be environmentally safe.
Electric discharge assisted mechanical milling (EDAMM) is a new and exciting materials processing technique which combines the attributes of conventional mechanical milling with all effects generated by electric discharges. It is demonstrated that EDAMM can be used to synthesize a range of functional materials in a matter of minutes, rather than hours or days. This report provides an overview of recent development of EDAMM method and it's application in rapid materials processing and synthesis of functional materials and their applications.

1. INTRODUCTION

John Benjamin and his colleagues at the Paul D. Merica Research Laboratory of the International Nickel Company (INCO) for the first time in 1970 used a high-energy attritor grinding mill designed for paint and ink production to process powders of nickel, chromium and a Ni-Al-Ti master alloy with dispersoid powders of thorium oxide and yttrium oxide to produce oxide-dispersion strengthened (ODS) superalloys [1,2].

This new high-energy milling process differed from conventional ball milling, which is used for mixing or comminution. During mixing the particle size, shape and composition is unaltered. When using a ball mill for comminution, the particle size is reduced by fracture, without any change in particle composition or significant plastic deformation of the particles. However, the high-energy milling process developed by John Benjamin, which he called "mechanical alloying", not only resulted in particle fracture but also heavy plastic deformation and welding [1,2]. Thus, mechanical alloying as it was described by Benjamin, differs from conventional ball milling in that the kinetic energy of the grinding media is sufficiently high to cause mechanically induce solid-solid, solid-liquid and solid-gas reactions between different species. Since John Benjamin discovery "mechanical alloying" became a widely used materials processing method. As the science of milling has progressed, a range of conventional and new milling and attriting devices have been developed [3-7]. However in all milling devices developed till now particles are generally mechanically deformed, fractured and cold weld using some combination of shearing and impact. It is commonly recognized that serious drawback of this technology is lengthy process time from few to hundreds of hours. It has been shown recently that the kinetics of mechanical milling (alloying) process can be dramatically speed up (from hours to minutes) by using electric discharges [8].

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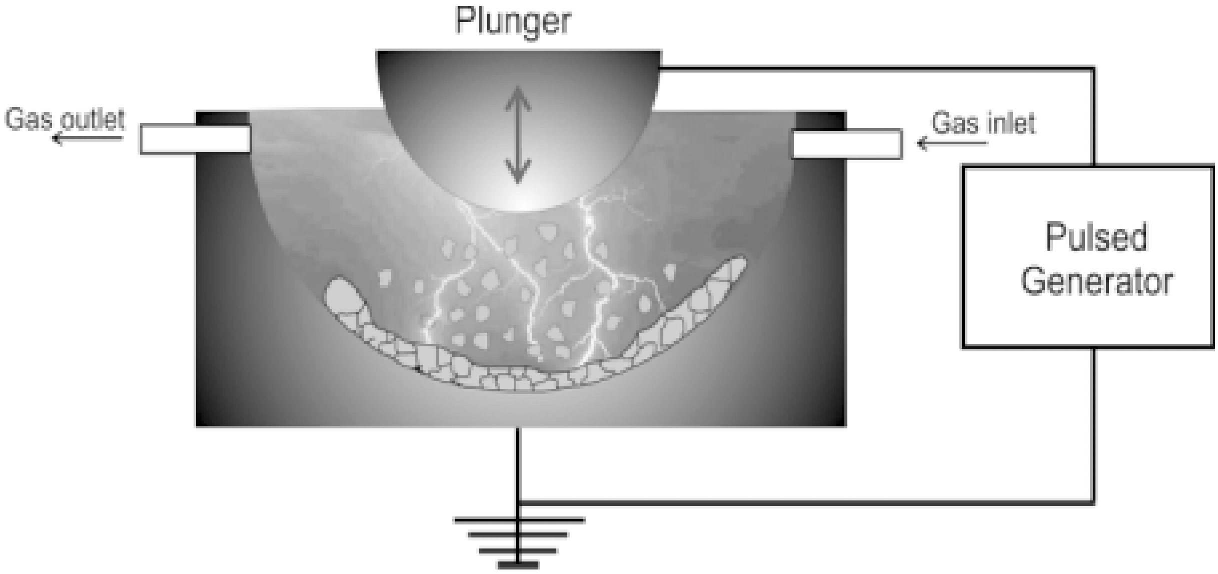

Fig. 1. Schematic of the electrical discharge milling device operating under flowing gas with pulsed DC power supply.

In this study we report on a new, rapid synthesis of functional materials by Electric Discharge Assisted Mechanical Milling (EDAMM) method [8].

2. EXPERIMENTAL

Stoichiometric amounts of powders (99% purity) to form were first mechanically pre-mixed in a laboratory mill for 30 min under a high purity argon atmosphere. Electric discharge assisted ball milling was performed in a modified vibrational laboratory rod mill. The mill was designed to produce a milling mode that combines repeated impact of a hardened curved rod end on powder particles, placed on a vibrating hemispherical container under electrical conditions of pulsed arc discharges (Fig. 1). The electric discharges were generated during milling in the gaps between the vibrating mill base, the powder particles and a loosely suspended conducting plunger. The power supply used in this study generated radio frequency impulses within the kV/mA range. During vibration, small gaps between the stainless steel rod and the chamber wall resulted in an electric discharge (Fig. 1). Milling was carried in a high purity Ar flowing at a rate of 0.3 m^3/min. In most of experiments a milling time of 10 min was used. X-ray diffraction (XRD) analysis of the as-milled powders was performed using a Phillips PW1730 diffractometer with a graphite monochromator and CuK_α radiation. Phase identification was carried out using the International Centre for Diffraction Data (JCPDS-ICDD 2000) powder diffraction files (PDF). The morphology of the powders was observed by a Leica 440 Stereoscan scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

EDAMM combines the benefits of producing fine, highly reactive particles via mechanical milling [4], with the interaction between accelerated ions and powder particle surfaces resulting from the use of electric discharges. During EDAMM, powders are subjected to a localized and intense reaction area characterized by the formation of an electrical discharge and/or plasma with parallel mechanical mixing/milling action.

This process is different from mechanical alloying processes which have been employed previously for materials processing. EDAMM is also different from the popular spark plasma sintering (SPS) used to rapidly sinter ceramic materials and other thermal plasma techniques that have used high-intensity arcs (ac or dc) and high-frequency discharges (RF and microwave) to synthesize various materials.

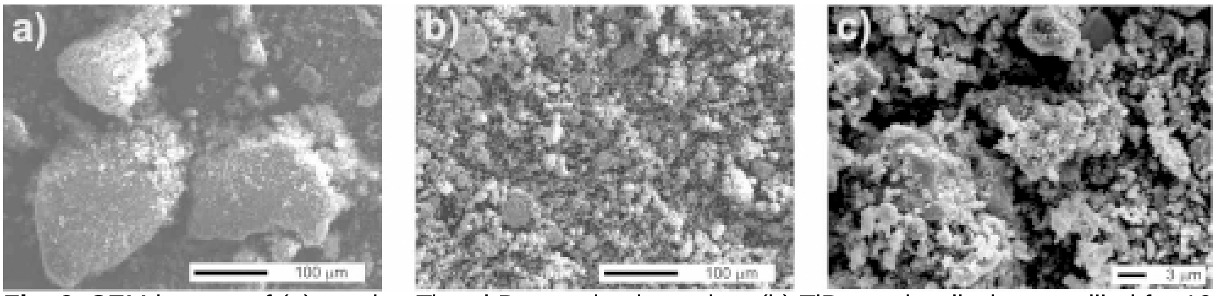

Fig. 2. SEM images of (a) starting Ti and B pre-mixed powders (b) TiB powder discharge milled for 10 minutes (c) Ti powder discharge milled in N_2 for 10 minutes.

The essential feature of our device is the control of the reaction temperature by controlling thermal discharge energy using a power supply working in the impulse mode. The discharge energy (and discharge temperature) is proportional to the impulse duration time. At low thermal energies (low temperature plasma) chemisorptions occur which is favorable for generation of gas-solid reactions (synthesis of hydrides and nitrides) while at higher thermal energies (higher temperature plasma) conditions are more favorable for solid-solid reactions (synthesis of hardmetals, compounds and reduction processes).

Plasma temperature and local density are widely regarded as two parameters that could significantly affect the powder formation and growth mechanism. The processing plasmas in our device are not clean; instead we have dusty, complex plasma-the presence of atomic, molecular, and ionic species which additionally complicate the understanding of the plasma environment. Although the processes occurring during EDAMM are not well understood experimental results obtained so far indicate that range of functional materials can synthesised within minutes.

Synthesis of hardmetals

The transformation of elemental metal powders into carbides and nitrides can by completed within 2 to 10 minutes. Our work shows that hardmetals can be rapidly formed as a result of the direct reactions between metals and B, C, and N_2. The following compounds were synthesised: TiB [9], B_4C, WC, ZrC, VC, TiC and TiN [10]. Fig. 2 shows SEM micrographs of starting powder (Fig. 2a) and milled after 10 min. The typical particle evolution during EDAMM is illustrated in Fig. 2. Fig. 2a illustrates microstructure of mixture of irregular large Ti particles and small boron particles. Milling time up to 10 min causes formation of large number of particles about 2 mm in size (Fig. 2b) predominantly in the form of agglomerates. Fig. 2c shows micrographs of TiN powder synthesised after 10 min milling of Ti in nitrogen.

Synthesis of functional oxides

$LiFePO_4$ is a promising environmentally friendly and low cost alternative cathode material for use in lithium-ion batteries. The most common materials production process used to manufacture $LiFePO_4$ is solid-state synthesis which entails several grinding and recalcination steps, occurring over many hours. High purity $LiFePO_4$ can be rapidly synthesised within 10 minutes from pre-mixed stoichiometric amounts of Li_2CO_3 (99%, Aldrich), $FeC_2O_4 \cdot 2H_2O$ (99%, Aldrich), and $(NH_4)H_2PO_4$ (97%, Aldrich) powders [11]. This result represents a significant advantage over conventional synthesis techniques that are often complicated and time consuming. Although the formation mechanism during discharge milling is not clearly understood it should be possible to fine-tune the crystallinity, particle size and shape, or surface characteristics of $LiFePO_4$ to produce any desired combination of properties. Furthermore, different precursor materials can potentially be used for synthesizing $LiFePO_4$ by electric discharge assisted milling. These precursors may be simply a more economically viable choice or involve additives or dopants to the precursor mix that will improve the inherent

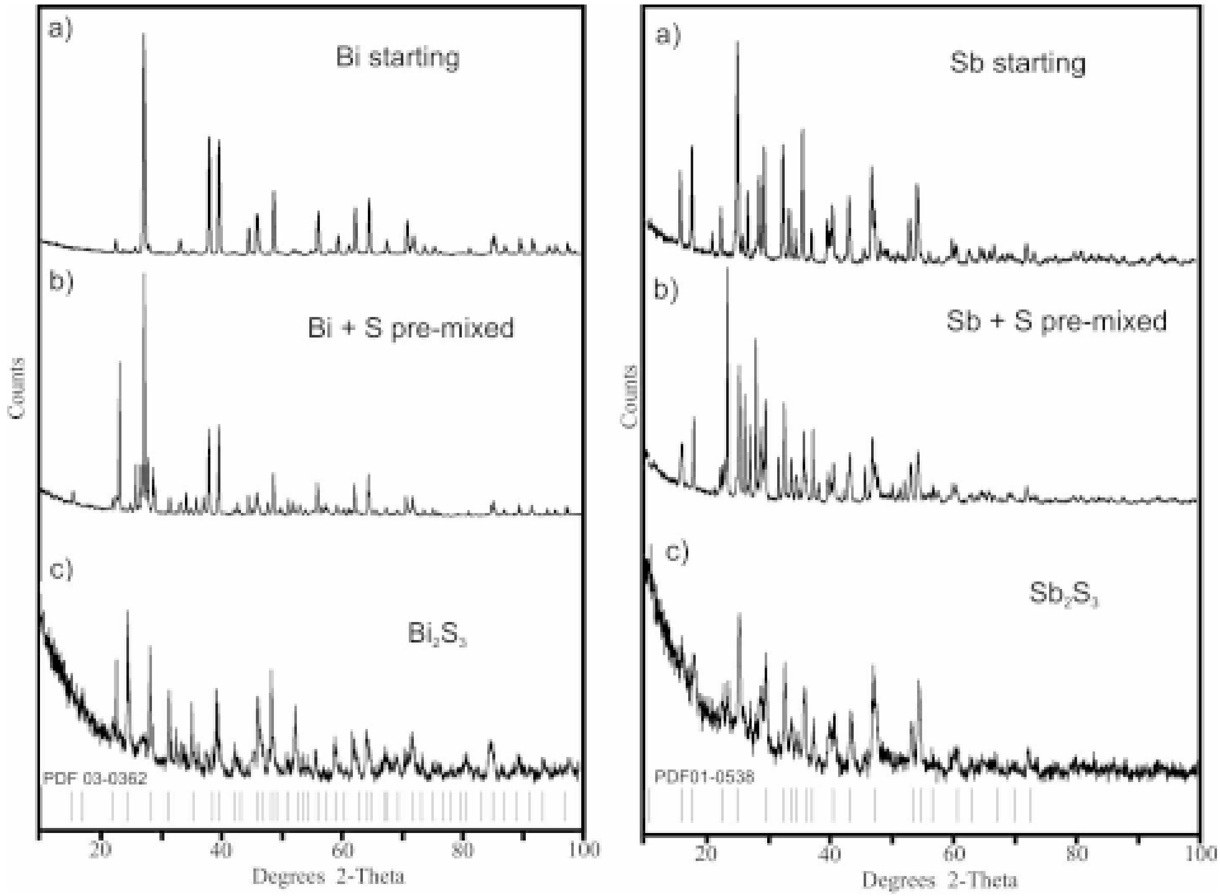

Fig. 3. XRD patterens of (a) starting powders, (b) powders after mechanical mixing and (c) sulfides powders produced by EDAMM.

poor conductivity of pure $LiFePO_4$. Moreover, EDAMM may facilitate the production of functional oxides and hydrides for use in energy storage applications that have been thought impossible to synthesize or require very time consuming preparation.

Synthesis of Bi and Sb sulfides

Binary metal sulfides show many important physiochemical properties which makes them attractive for a wide range of commercial applications. Group V-VI binary sulfides are semiconductors, and find photovoltaic applications in cameras, thermoelectric devices, IR spectroscopy, and many electronic and optoelectronic devices. Powder metal sulfides have been used in the following applications: batteries, lubricants and lubricant additives, pigments, photovoltaic materials, infrared filters, and sputtering targets. Sb and Bi sulfides can be synthesised by a number of methods. They can be produced by direct reaction with sulphur vapour in a vacuum, thermal decomposition, solvothermal reactions, and other chemical approaches. However, the evaporation and direct elemental reaction methods show difficulties in obtaining exact stoichiometric compositions, and the final products often show amorphous structures. As a consequence, additional high temperature processing is required to crystallise the sulfide. All thermal decomposition methods require high temperatures, and the disadvantage of these methods is that the final product contains impurities. Solvo-thermal synthesis often requires the use of toxic solvents, and this limits their use. EDAMM process can be successfully used to generate reactions between metal and sulfur to form metal sulfide. After pre-mixing in conventional ball mill, both the Bi+S and Sb+S mixtures were processed by EDAMM. After 10 min powders exhibit full reaction to Bi_2S_3 and Sb_2S_3. This reaction time is significantly shorter than has been reported for other synthesis techniques. In addition, this processing technique does not require the use of toxic chemicals. The sulfide powders produced by EDAMM had a particle size larger than is usually found after different synthesis techniques of around 2 mm. These small particles tended to form large agglomerates of up to 20 μm in diameter during EDAMM [12]. Fig. 3 shows XRD results of starting powders, premixed and after EDAMM.

Reduction and exchange reactions

Since the temperatures in thermal plasma are extremely high (>10^4K), chemical reactions are much more energetic than those encountered in conventional processes therefore, thermal plasma offer an attractive route for generation of reduction and exchange reactions. Conventional thermal plasma devices are high intensity arcs in which reactants flow through the device. Chemical reactions occurs during the flow in plasma flame which limits reaction time. EDAMM method is ideal for producing reactive plasmas. In our device there is no limit of the residence time of materials in the plasma, the plasma temperature is controlled by controlling impulse duration time and amplitude. Also constant mechanical agitation of the powder inside the chamber induces powder particle fracturing/fragmentations and generation of new atomically clean surface which additionally speeds up the reaction rate. In our study the following experiments were performed.

Discharge milling of hematite for periods of up to 20 minutes in Ar/3%H_2 resulted in the formation of magnetite after 10 minutes and subsequently formation of mixture of pure iron and FeO_x phases after 20 minutes milling [13].

Discharge milling in Ar of ilmenite powder ($FeTiO_3$) pre mixed with graphite resulted in formation of composite TiC + Fe_3C [14] after 5 minutes of milling.

PbS and Sb_2S_3 have been successfully reduced with both Fe and Mg after EDAMM for 5 minutes in Ar.

4. CONCLUSIONS

It has been shown that functional materials in the powder form can be produced within minutes using electric discharge assisted mechanical milling.

Reported results show a significant advantage of this method over conventional synthesis techniques that are often complicated and time consuming. EDAMM may facilitate rapid production of functional materials for use in many applications that have been thought impossible to synthesize or require very time consuming preparation.

REFERENCES

[1] J.S Benjamin // *Metallurgical Transactions* **1** (1970) 2943.

[2] J.S Benjamin // *Scientific American* **234** (1976) 40.

[3] H. Roz // *Mater. Sci. Forum* **179-181** (1995) 419.

[4] C.C.Koch // *Annu. Rev. Mater. Sci.* **18** (1989) 121.

[5] A.Calka and B.Ninham, *US Patent, 35383615, WO 9104810.*

[6] A.Calka and A.P.Radlinski // *Mater Sci Eng A* **134** (1991) 1350.

[7] D. Bassest, P.Matteazzi and F. Mani // *Nater. Sci and Engineering A* **168** (1993) 149.

[8] A. Calka and D. Wexler // *Nature* **147** (2002) 419.

[9] A.Calka and D.Oleszak // *Journal of Alloys and Compounds*, in press.

[10] A.Calka, unpublished results.

[11] S.A. Needham, A. Calka, G.X. Wang, A. Mosbah and H.K. Liu // *Electrochemistry Communications* **8** (2006) 434.

[12] A.Calka, A.Mosbah, N. Stanford and P.Balaz // *Journal of Alloys and Compounds*, in press.

[13] D. Wexler, A. Calka and D. Dunne // *Journal of Metastable and Nanocrystalline Materials* **26** (2005) 16.

[14] A.Calka, D. Oleszak and N. Stanford // *Journal of Alloys and Compounds*,in press.