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State of the Art of Research on Mechanochemical Processing and Mechanical Alloying in Korea

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The activation of chemical reactions by milling reactants in a ball mill is a unique characteristics of mechanochemical processing (MCP). While particle sizes generally decrease to the micrometer level during MCP, fine grains in the nanometer range are developed within each particle. These nanograins enhance the reaction kinetics, activating chemical reactions which otherwise require high temperatures to occur. Moreover, product powders usually have high sinterability and catalytic effect, mainly due to high level of internal and external defects. Other advantages of MCP include the homogeneity of product powders and suitability for the low cost, large scale production of various nanopowders.

A wide range of advanced materials including nanopowders have been recently synthesized by MCP and mechanical alloying in Korea and they include structural composites such as nanocomposite hardmaterials and heat resistant materials, active cathode and anode materials for Li-ion batteries, nanostructured metal hydrides for hydrogen storage, magnetic materials, and biomaterials. A brief review on these research activities in Korea will be presented together with some results of the recent works on the synthesis of nanocomposite powders by MCP in our own laboratory.

Key words; mechanochemical processing, high-energy ball milling, nanocomposite powder

1. INTRODUCTION

Developed originally for the production of oxide-dispersion strengthened (ODS) nickel- and iron-based superalloys[1,2] for applications in the aerospace industry, the focus of mechanical alloying (MA) had been on amorphous and nanocrystalline materials, but the interest is now shifting towards mechanochemistry and MCP of nanoparticles[3,4], nanocomposite powders[5-9], and even solid state transformation of complex compounds[10] and organic materials[11,12] have been reported recently.

During milling, plastic deformation, fracture, and cold welding of reactant particles occur repeatedly by collisions among milling balls as well as between balls and container walls. The accumulation of shear bands initially promotes plastic deformation inside particles and then decomposes into sub-grains delineated by low-angle boundaries. Further milling decreases the sub-grain size and eventually become randomly oriented by high angle grain boundaries. As the particle size decreases to the micrometer range, a nanometer grain size is developed within each particle. This extremely fine grain enhances the reaction kinetics, inducing chemical reactions which otherwise require high temperatures to occur during milling at ambient temperature. This is one of the unique features of mechanochemical processing.

This review presents an overview of the research activities in mechanochemical processing and mechanical alloying in Korea as well as the recent works of our own laboratory in this field.

2. STRUCTURAL MATERIALS

2.1 Hardmaterials nanopowders

In general, TiC-base cermet alloys are used as cutting tools for the finishing works of steel and cast iron due to their high hardness and abrasion resistance characteristics. To achieve a fine microstructure, expensive TiC powders of very fine particle size are used. One of the promising routes to produce inexpensive ultra-fine TiC base cermet powders is to utilize MCP starting with Ti, Ni and C powders. Choi[13] used both high- (SPEX-8000) and low-energy (horizontal ball mill) ball mills to synthesize very fine TiC-Ni cermet powders of 0.2-1.5μm compared with 3-5μm commercial cermet powders. Fig. 1 shows that the elemental Ti and C powders were reacted to form TiC after about 2 hours.

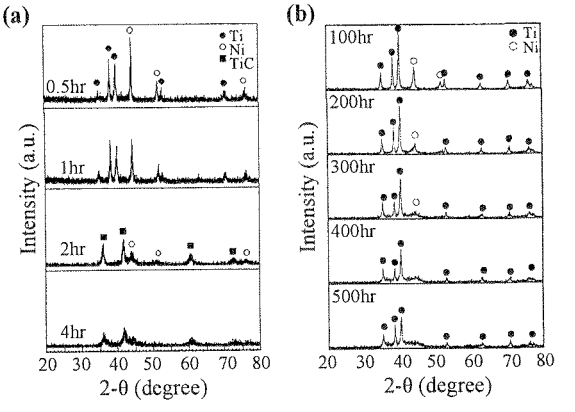

Fig. 1. Change of XRD patterns with milling time for Ti-Ni-C composite powders by (a) SPEX-8000 mill and (b) conventional low energy ball mill[13].

The sintered body of a TiC-base cermet alloy comprises a distinctive dual structure, known as the core-rim structure, in its carbide grains. Fig. 2 shows, however, an ultra-fine TiC-base cermet alloy with a homogeneous solid solution grain structure that does not comprise a typical core-rim structure in the carbide grain. This uniform microstructure within carbide grain was obtained by using a mixture of TiC-Mo_2C-Ni nanocomposite powder prepared by MCP with an advanced planetary ball mill in our laboratory recently [14].

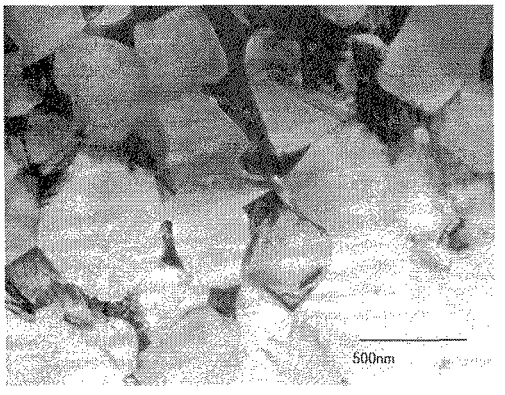

Fig. 2. TEM image showing homogeneous solid solution grain structure instead of a typical core-rim structure[14].

Song et al.[15] have also used SPEX-8000 mill to prepare nanostructured $MoSi_2$-TiC composite powders. (see Fig. 3) They observed an abrupt increase of vial surface temperature due to a sudden reaction between elemental powders during milling. They concluded that the reaction between Ti and C largely controls the overall reaction to form $MoSi_2$-TiC composite powders.

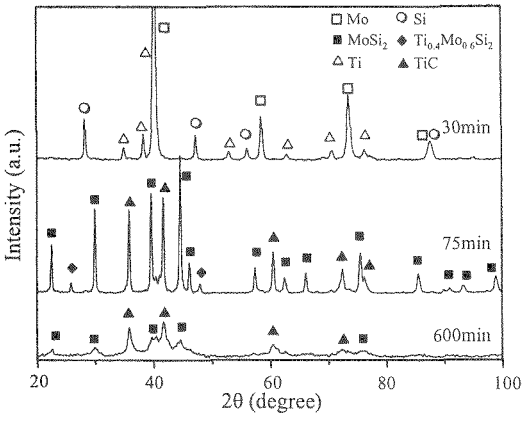

Fig. 3. XRD patterns of $MoSi_2$+TiC powders with milling time[15].

Shim et al.[8, 9] have carried out a series of experiments to study a so-called mechanically activated self-sustained reaction (MSR) with Ti+Si_3N_4 and Ti+BN powder mixtures. Both the reactions proceed on MSR as predicted by thermodynamic calculations and the incubation time was not longer than about 2 hours in both cases (see Fig. 4).

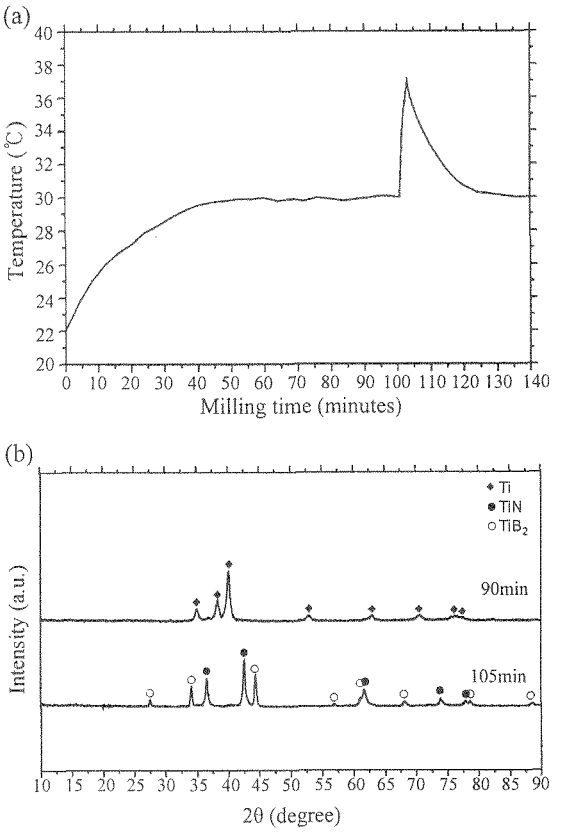

Fig. 4. Indications of mechanically activated self-sustained reaction (MSR) in Ti-BN powder mixture[8].

Recently, we have studied the effect of stearic acid as a process control agent (PCA) on the mechanochemical reaction between Ti and BN powders[16]. On the contrary to the result without PCA, they could change the reaction mode from abrupt MSR to gradual reaction type, resulting in much more fine TiB_2 crystalline size of less than 40 nm compared to several hundred nanometer in the case without PCA addition (see Fig. 5).

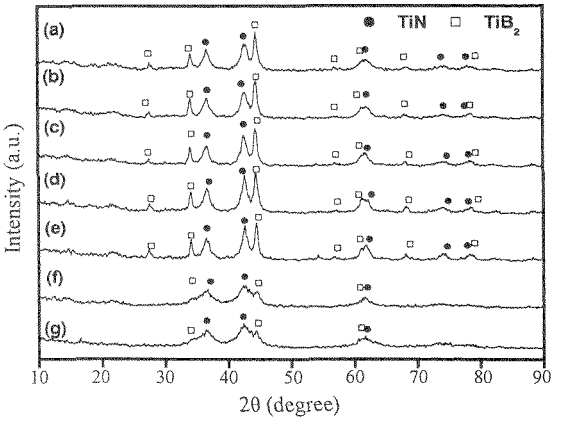

Fig. 5 XRD patterns of Ti+BN powders milled for 16 hours with (a) 0, (b) 0.5, (c) 1.0, (d) 1.25, (e) 1.375, (f) 1.5 and (g) 1.75 wt% stearic acid[16].

Nanocrystalline WC powders have been prepared from W and carbon black powders with SPEX-8000 mill by Cha[17]. They reported that WC started to form after 10 hours and the formation reaction of WC was almost completed after about 24 hours of milling (see Fig. 6). They also found that the grain size was much finer than that prepared by a spray conversion process. We have also prepared WC from W and graphite powders with both SPEX-8000 and Fritsch P7 planetary mill[18]. As shown in Fig. 7, the WC formation reaction was completed in less than 4 hours with Fritsch P7 at the same BPR (10:1) as the one adopted by Cha[17]. However, it took more than 20 hours with SPEX-8000 mill. These results indicate that the mode of milling, normal collision or a mix of shear and normal collision may have significant effect on the mechanochemical reaction for some reaction systems.

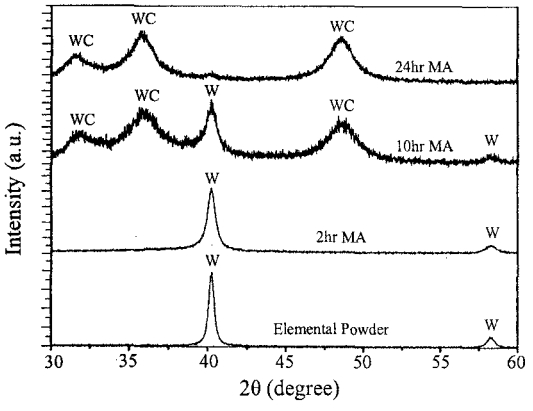

Fig. 6. XRD patterns of W+C powder mixtures with milling time[17].

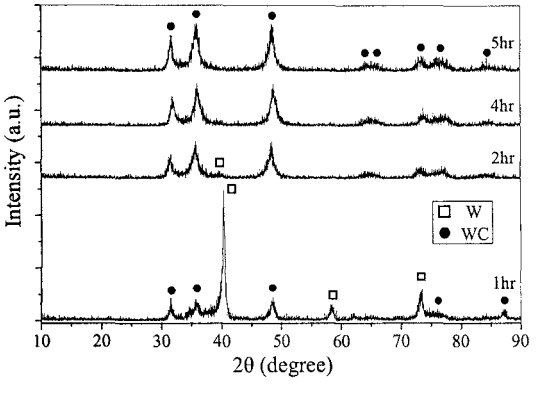

Fig. 7. XRD patterns of W+C+Cr+V powder mixtures with milling time[18].

MCP has also applied to prepare solid solutions of TiN-AlN starting from mixtures of cubic TiN and hexagonal AlN powders. As shown in Fig. 8, it is estimated that up to about 25 mol% AlN could be dissolved into the NaCl type TiN structure after 16 hours of milling by SPEX-8000. This result confirms that a metastable solid solution can be prepared by high energy ball milling even a mixture of rather stable compounds near ambient temperature.

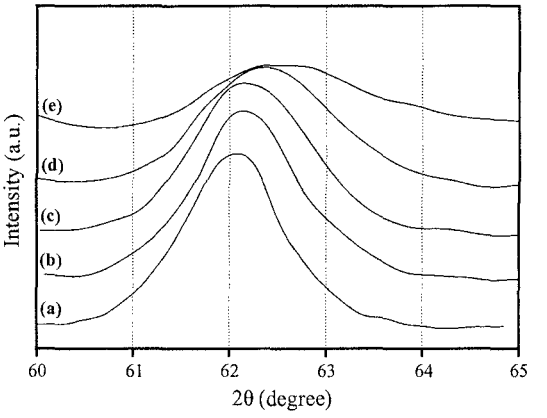

Fig. 8. TiN(220) peaks in XRD patterns of powders (a) 0, (b) 25, (c) 33, (d) 50, and (e) 75 mol% AlN milled for 16 hours[19].

Recently, we have synthesized TiN particulate-Ti_5Si_3 matrix nanocomposite powder from a mixture of Ti and Si_3N_4 powders by MCP[20]. The composite powder was formed by a displacement reaction between Ti and Si_3N_4 during milling and the reaction proceeds in a MSR form. Just after MSR, it consists of TiN crystallites of a few hundred nanometers embedded into a Ti_5Si_3 matrix and the size of TiN decreases down to 5 nm after 20 hours of milling (see Fig. 9).

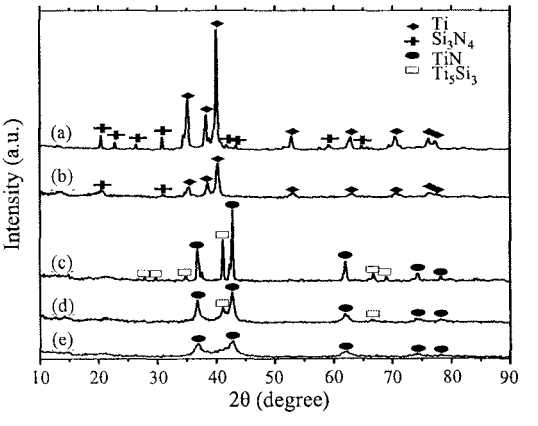

Fig. 9. XRD patterns of Ti+Si_3N_4 powders milled for (a) 0, (b) 90, (c) 100, and (d) 1200 minutes[20].

2.2 Heat resistant materials

Hong[21-23] have studied the effect of mechanical milling on the relative density after sintering and the grain size of mechanically alloyed 93W-5.6Ni-1.4Fe+0.1-5 wt% Y_2O_3. They have used a conventional tumbling ball mill and the milling time was up to 72 hours. The grain size of W after sintering at 1300℃ for 1 hour decreases and the relative density increases with milling time (see Fig. 10). They could obtain ultra-fine tungsten particles of about 3㎛ with about 99% relative density by a simple MA process.

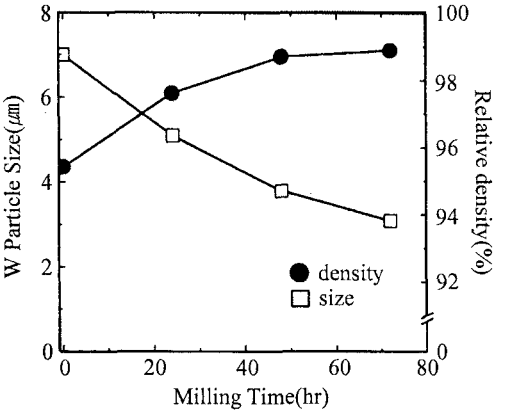

Fig. 10. Variation of tungsten particle size and relative density of 93W-5.6Ni-1.4Fe alloy with milling time after solid state sintering at 1300 for 1 hour[23].

3. FUNCTIONAL MATERIALS

3.1 Electrode materials for secondary batteries

Although majority of research works on MCP in Korea had been concentrated upon structural materials in the past, more researchers are now studying MCP of functional materials, such as active electrode materials for metal hydride and Li-ion secondary batteries as well as hydrogen storage materials, magnetic materials, and even biomaterials.

Jeong[24, 25] have prepared $LiCoO_2$ precursor powder from a mixture of $LiOH{\cdot}H_2O$ and $Co(OH)_2$ powders by milling with SPEX-8000D. They could obtained highly crystallized HT-$LiCoO_2$ by subsequent firing the precursor powder at 600℃ for 2 hours, which is a much improved firing condition compared with the conventional solid state reaction between lithium carbonate and cobalt oxide powders. Fig. 11 shows the discharge cycle behavior of MA treated powder together with conventional powders (designated as SM).

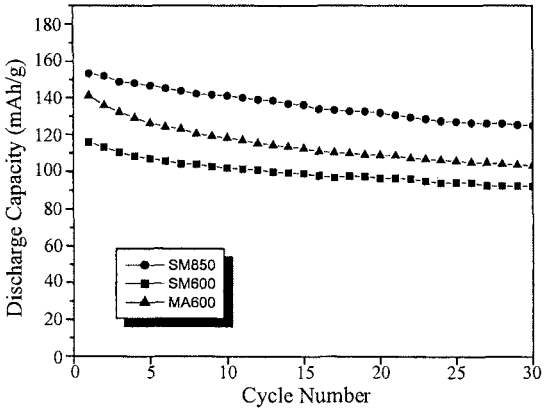

Fig. 11. Discharge capacity as a function of cycle number for $LiCoO_2$ cycled between 3.0 and 4.2V at the C/10 rate[25].

Mechanical milling can be applied to improve the cycle life of Mg_2Ni[26] and Ti-Zr-V-Mn-Ni electrode[27] by coating the surface of them with Ni or graphite. The cycle life of both electrodes were significantly improved by mechanical coating as shown in Fig. 12 and 13.

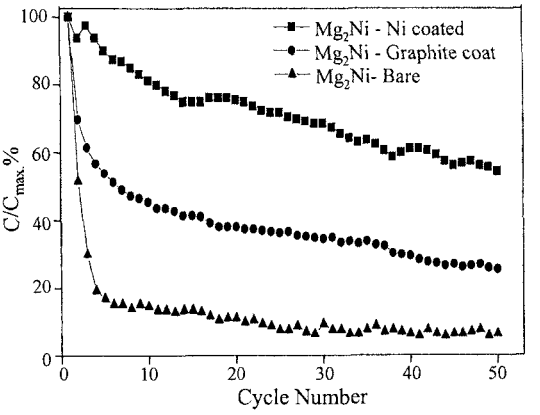

Fig. 12. Cycle life of Mg_2Ni electrodes mechanically coated with nickel and graphite compared with bare electrode[26].

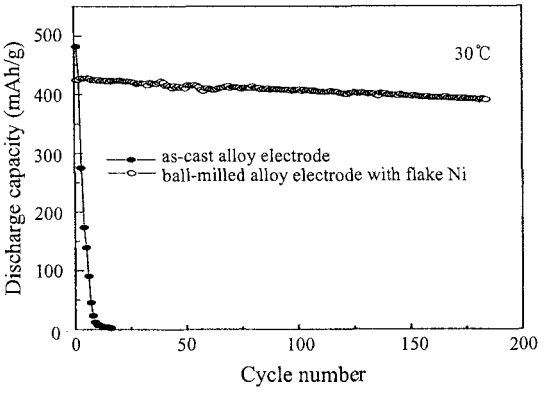

Fig. 13. Comparison of cycle life of as-cast and ball-milled alloy with Ni flake[27].

3.2 Metal hydrides for hydrogen storage

MA can also be applied to disperse fine catalysts homogeneously in high capacity hydrogen storage materials such as MgH_2. Song[29] have applied a reactive mechanical milling process to improve the hydrogen sorption properties of Mg. They have found that milling Mg powder with 10 wt% oxide powders under high hydrogen pressure increases the hydriding rate significantly (see Fig. 14) mainly due to decrease in Mg particle size.

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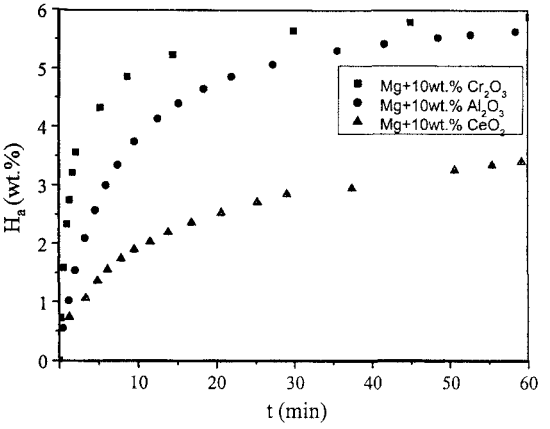

Fig. 14. Variation of weight percentages of hydrogen Ha (wt%) with time for the first cycle of hydriding at 573 K under 11 bar H_2[29].

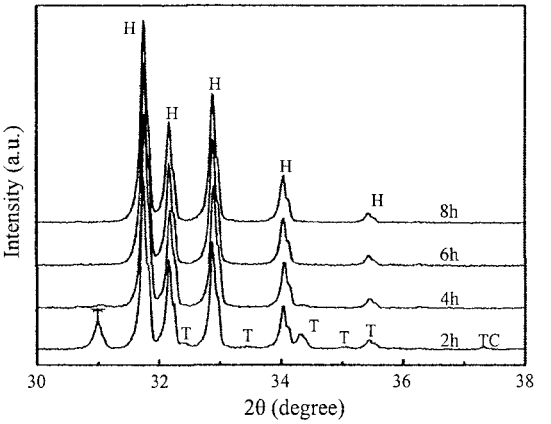

Fig. 16. XRD patterns of $Ca_2P_2O_7$+$CaCO_3$ powder milled for each time period and then heat-treated at 1100 for 1 hour[31].

3.3 Giant magnetocaloric materials

We have recently synthesized magnetocaloric materials, $MnFeP_{1-x}As_x$, from Mn+Fe+P+As powders by MCP with SPEX-8000 mill[30]. It has been found that a MSR occurs within 2 hours of milling and that very fine polycrystalline powder having a hexagonal Fe_2P structure could be obtained just after MSR. This result confirms that even complex crystal structures could also be formed by MCP near room temperature.

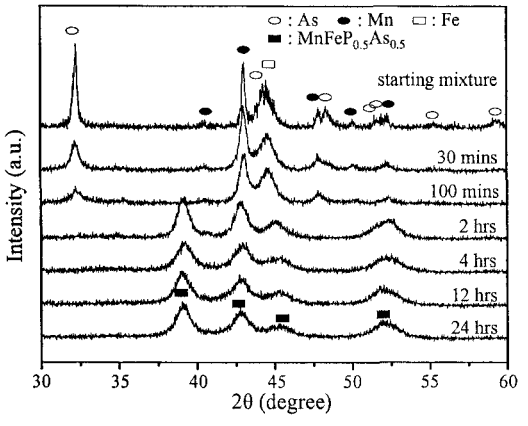

Fig. 15. Change of XRD patterns of Mn+Fe+P+As powders with milling time[30].

3.4 Biomaterials

Finally, it has been reported by Rhee[31] that high crystalline hydroxyapatite powders can be obtained by simple milling of calcium phosphate and calcium carbonate with subsequent heat treatment. They suggested that the hydroxyl group needed to form hydroxyapatite during the heat treatment might have been supplied from the mechanochemical reaction between the starting powders and water during milling.

SUMMARY

The present review on research activities in application of MCP in Korea clearly shows that MCP now becomes a versatile tool to prepare high performance powders for various structural applications such as hard metals, cermets, and heat resistant materials. It can also be successfully applied to functional materials such as electrodes for secondary batteries, hydrogen storage, and even for biomaterials. Other promising applications for MCP are mechanically induced solid state transformations in complex compounds and mechanochemical transformations of molecular materials such as organic materials.

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