

Mechanical alloying for electrochemical applications

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In the last few years, mechanical alloying has become an important field of research in materials science. The mechanical alloying technique consists in inducing a solid state reaction between the components of an initial powder mixture by repeated mechanical deformations caused by ball-powder-ball collisions using high-energy ball mill. Numerous structural defects are created which increase the interdiffusion of the elements. Strain is introduced in the lattice and as a result, crystals fracture into smaller pieces down to a nanometer range. The growing interest for this technique is due to the possibility of obtaining, easily and at a low cost relative to some other techniques, materials with unique chemical, physical and mechanical properties. Thus, ball milling process has been successfully applied to the synthesis of various materials such as nanocomposite materials, metastable alloys, amorphous compounds and nanocrystalline materials. These materials have already given rise to great interest in many applications including oxide dispersion strengthened alloys and intermetallics for aircraft engines, ceramics for high temperature applications, nanocrystalline alloys for hydrogen storage and more recently advanced materials for electrochemical applications.

Advantages and limitations of the ball-milling technique for electrochemical applications will be illustrated through different examples taken from studies performed in our laboratories at INRS-EMT:

- *Advanced metal hydrides for Ni-MH batteries [1-4].* It was recently found that some amorphous or nanocrystalline Mg-based alloys prepared by mechanical alloying can absorb and desorb electrochemically a large amount of hydrogen at room temperature. For example, amorphous and metastable MgNi alloy obtained after 10 hours of mechanical alloying using a vibratory mill has an initial discharge capacity of about 520 mAh/g compared to 280-320 mAh/g for commercial LaNi₅-based alloys. This amorphous electroactive material can also be obtained in large scale (1 kg of alloy per batch) using an industrial high-energy attritor. The great enhancement of the properties of these anode materials could be explained by the disordered character of the amorphous structure, which provides numerous desirable sites for electrochemical hydrogen storage. Further milling results in a partial crystallization of amorphous MgNi into nanocrystalline MgNi₂ and Mg₂Ni, which decreases significantly the electrode performance. Moreover, carbon added at the beginning of the milling to avoid excessive powder welding, in spite of its small proportion (1 wt.%), has a deleterious influence on the performance of the electrode material.

- *New cathode material for the chlorate industry [5-10].* The cathodic overpotential associated with the hydrogen evolution reaction constitutes the main electrochemical energy loss in the production of sodium chlorate. In collaboration with several industrial partners, we have conceived a new cathode material for the chlorate industry leading to a considerable reduction of the cathodic activation overpotential. Moreover, the electrode does not show any sign of degradation after prolonged electrolysis

tests. This new electrocatalyst consists of nanocrystalline and metastable Ti₂RuFeO₂ alloy prepared by mechanical alloying. This material can be deposited onto large substrates required for industrial application by vacuum plasma-spray.

- *Improved corrosion resistance materials [11-12].* Nanocrystalline Ru and Mg materials prepared by high energy ball milling exhibit a better resistance to corrosion in alkaline media than their polycrystalline counterparts. This could be related to the presence of numerous defects and grain boundaries created by the high-energy ball milling process, which may facilitate the nucleation of a dense and protective oxide-hydroxide film at the surface of the ball-milled particles.

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