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MWCNT as mechanical support during ball milling of an AB_5 alloy used as negative electrode of a Ni–MH battery

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ABSTRACT

The $La_{0.8}Cm_{0.2}Ni_{3.8}Co_{0.3}Al_{0.4}$ (AB_5) (Cm: Cerium rich misch metal) alloy was mechanically mixed with carbon nanotubes at four different time periods, in order to study the effect on the mechanical milling and the electrochemical performance of the negative electrode of a Ni-MH battery. The microstructure and size particle during processing was analyzed by X-ray diffraction. The morphology, examined by scanning electron microscopy, showed that the surface of the AB_5 alloy was modified by carbon nanotubes. The electrochemical properties of the obtained materials were measured and discussed.

Introduction

Among different available post-production processes, the mechanical milling is usually used to improve the kinetic of AB_5-type hydrogen storage alloys, due to the increase of the specific surface area and the hydrogen diffusion [1] [2]. It is also believed that mechanical milling increases the hydrogen sorption properties and facilitates the intermetallic activation [3]. However, several authors have reported a deficiency on the electrochemical performance when these alloys are subjected to milling processes. Lenain et al. [4] observed a reduction in the electrochemical discharge of an AB_5-type alloy along with high energy milling time. Joseph et al. [5] found that longer milling time of the $LaNi_5$ alloy results in the formation of an anomalous state of resistance sorption reactions, mainly due to the slight reduction in volume of the unit cell and the atomic disorder present in these systems. Ares et al. [6] reported that the appearance of an amorphous phase during milling of the $LaNi_5$ alloy produces a detrimental effect on the discharge capacity and kinetics when compared with the nanocrystalline phase.

The electrochemical discharge capacity of the alloy is strongly related to the surface condition and the crystal structure (crystallinity vs. amorphism), because the atomic hydrogen released at the charge transfer process in the electrolyte/alloy interface must firstly be adsorbed on the surface of the intermetallic and then proceed to the formation of the hydride. According to previous studies [7], the grinding time has an important role in the microstructural and sorption

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properties of the intermetallic, where CNTs could function as mechanical support due to their ability to deform and remain in the elastic range over high deformation efforts [8], and absorb part of the energy produced by the mechanical grinding.

In this paper the effect of milling time on the structure and electrochemical properties of an AB_5-type alloy, milled with and without nanotubes, was analyzed. The aim of the work is to analyze if the use of CNTs could preserve the discharge capacity during the milling of the alloy.

Experimental

The characterization and purification process (using H_2SO_4 3 M) of the multi-walled carbon nanotubes (MWCNT) used during the milling process can be found in previous research [9].

The $La_{0.8}Cm_{0.2}Ni_{3.8}Co_{0.3}Al_{0.4}$ (AB_5) alloy was made by melting pure metals in an induction furnace [10]. The intermetallic alloy was mixed with and without CNTs by mechanical milling in an SPEX 8000D high energy miller. The process was performed with 3:1:0.1 and 3:1 for ball:alloy:CNTs and ball:alloy mass ratios for the alloy with and without CNTs, respectively; at four different times (10, 30, 90 and 120 min) in Ar atmosphere. Subsequently, the mixtures were pressed at 200 MPa together with Carbon Teflon (Carbon Black Vulcan XC72 + PTFE) in a Ni mesh used as mechanical support and electric current collector. The working electrodes had 11 mm diameter and about 1 mm thickness.

An open cell with a three electrodes configuration (Ni mesh as CE and Hg/HgO as RE) in a 6 M KOH aqueous solution as electrolyte, was used to measure the electrochemical properties. The charge/discharge cycling was studied at 0.5C current rate, the charge time was 20% plus the nominal equivalent capacity and the discharge cut-off potential was −600 mV. The high rate dischargeability was between 0.1C and 5C. All electrochemical studies were performed at room temperature.

The microstructural characterization was done in a Philips CM200UT High Resolution Transmission Electronic Microscope and a Philips PW3700 X-ray diffractometer. The crystallite size and the micro-strains were determined by the Rietveld method using the HighScore Plus 3.0 software. The CNTs-added electrodes were analyzed in a FEG NovaNano 230 Scanning Electronic Microscope (SEM).

Results and discussion

Fig. 1 compares the SEM images of the alloy samples mechanically milled with CNTs (a–d) and without CNTs (e–h), during four different periods of times. Some foamy agglomerates composed of small aggregated particles are observed. The analysis of agglomerate size distribution shows [11] that after 10 min of milling the alloy (Fig. 1-a), the agglomerate size distribution is between 20 and 30 microns, whereas for longer time periods it is between 10 and 20 microns (Fig. 1 b–d). Only after 120 min of milling, the agglomerates alloy surfaces present a smooth appearance. The milling of the alloy-CNTs

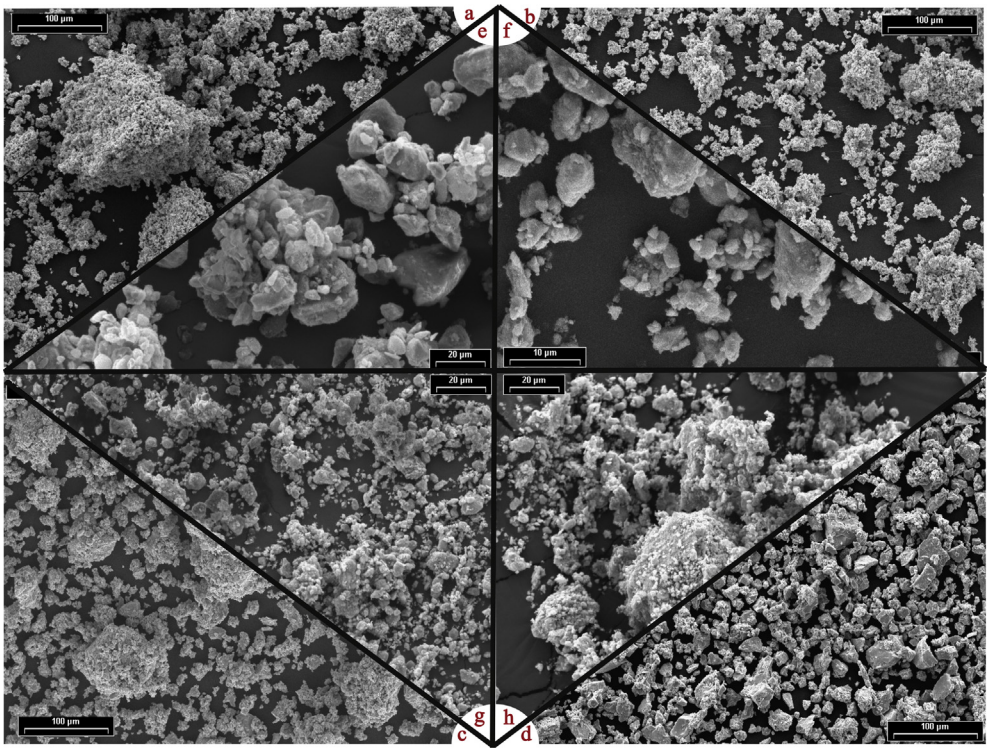

Fig. 1 – SEM images of mechanical milling of alloy (a–d) and alloy-CNTs (e–h), (10, 30, 90 y 120 min).

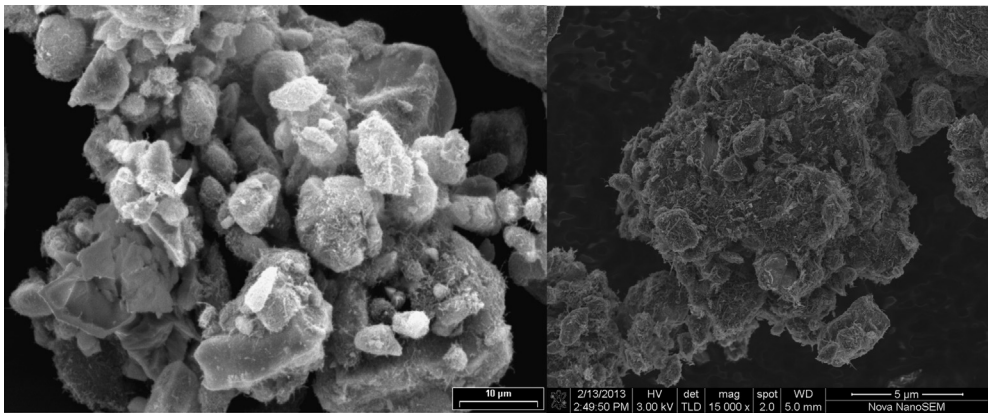

Fig. 2 – SEM images of mechanical milling of alloy-CNTs.

shows carbon nanotubes deposited on the surface of the alloy (Fig. 2). The milling of alloy-CNTs up to 30 min (Fig. 1 e–f) presents agglomerates that are between 10 and 20 microns, while for longer time periods, the agglomerates size is smaller than 10 microns.

In Fig. 3, the X-ray diffractograms of the milled alloy and the pattern (PDF 65–0093) are presented. The results show the presence of a homogeneous alloy with the $LaNi_5$-type phase. It has a direct correspondence with the $CaCu_5$-type hexagonal structure, which has the P6/mmm space group. The peak shift position in the comparison with the pattern indicates a change in the lattice parameters, caused probably by the substitution of the A and B sites in the alloy. Fig. 3 shows that no new phase formations were detected along milling. Neither can the nanotubes be seen after the grinding of alloy-CNTs, which is expected due to the low weight ratio compared with the alloy.

It can also be observed that the mechanical processing of the powders produced a widening of the diffraction peaks with increasing milling time, especially after 30 min of milling, where the peaks tend to be wider and overlap with the nearby ones.

The observed changes can be ascribed to the microstructural modifications introduced, such as defects, stresses, and others [12], and the crystallite size reduction resulting from the mechanical processing of the samples. The crystallite size dependence and the microstrain amount along milling time is reported in Fig. 4.

Fig. 4 shows the increase of micro deformations with the milling time. For the same milling time, the microstrains are always lower for CNTs-added than single alloy. After 120 min of milling, the single alloy presents 6% fewer micro-deformations than the one milled alone.

On the other hand, the crystallite size decreases rapidly in the alloy milled without CNTs, on the last time period the

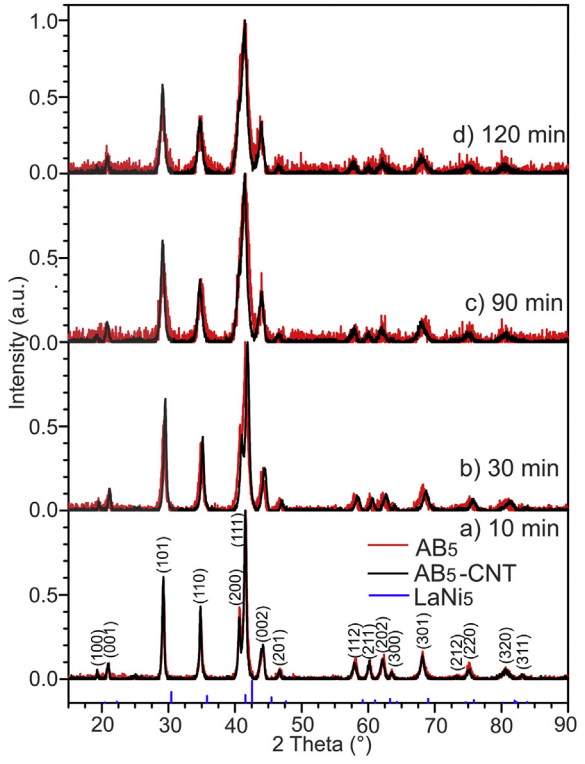

Fig. 3 – XRD of mechanical milling alloy and alloy-CNTs.

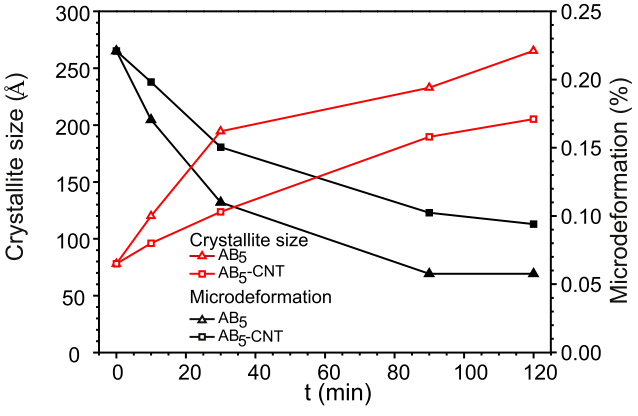

Fig. 4 – Crystallite size and microstrain percentage versus milling time.

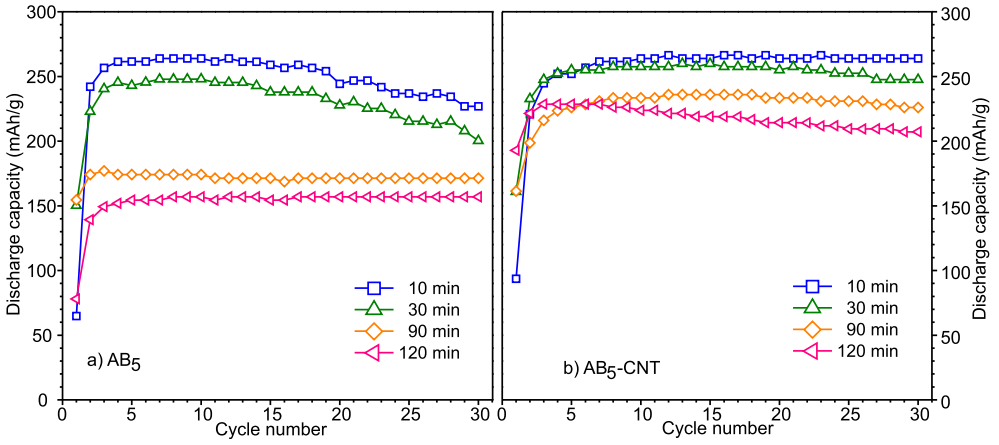

Fig. 5 – Discharging curves of working electrode made with a) alloy and b) alloy-CNTs, mechanically milled.

crystallite size reaches only about 26% of its initial size of 265 Å. The sample of the CNTs-added has a less severe decrease and at 120 min grinding, it becomes about 46% of its original size.

This result can be attributed to the coating of the metal particles with layers of nanotubes observed in the micrographs (Fig. 3). It is known that CNTs may act as extremely strong springs when exposed to small forces, and when they are subject to increased loads they may deform considerably and return to their original shape later [8], thus acting as a mechanical support during milling.

These results are reflected in the electrochemical tests, where negative electrodes prepared with CNTs-added have higher discharge capacity (C_d) than those prepared with the alloy milled alone. (Fig. 5).

The alloy with CNTs-added has a very close capacity for 10 and 30 milling times. While at 120 min it has 25% C_d higher than the alloy milled alone. C_d results for cycle 30 and the reduction rates for the alloy milled with and without nanotubes are presented in Table 1.

Fig. 6 compares the high rate dischargeability of the electrodes prepared with the milling of the alloy and alloy CNTs-added with rates between 0.1C and 5C.

At 10 min into the alloy milling, the C_d is slightly reduced at high dischargeability rates. However, this behavior is affected as the milling time increases. The performance at different rate discharges of the single alloy shows a steeper slope at longer milling times. After 120 min milling, the discharge capacity at 5C is 21% of the capacity presented at 0.1C.

The C_d of the electrode made with the CNTs-added alloy has a similar slope for all milling times, which is smaller than the one presented in the single alloy. The lower discharge capacities were obtained for the samples milled for 90 and 120 min where they reduced their capacity over 45% to 5C rate. However, it is interest to note that for times equal or greater

Table 1 – Capacity comparison of mechanical milling of AB_5 vs. AB_5-CNTs.

Milling time (min)	Capacity at 30th cycle (mAh/g)		Capacity reduction of AB_5 reference to AB_5-CNTs (%)
	AB_5	AB_5-CNTs	
10	227	264	14
30	200	248	19
90	171	226	24
120	157	207	24

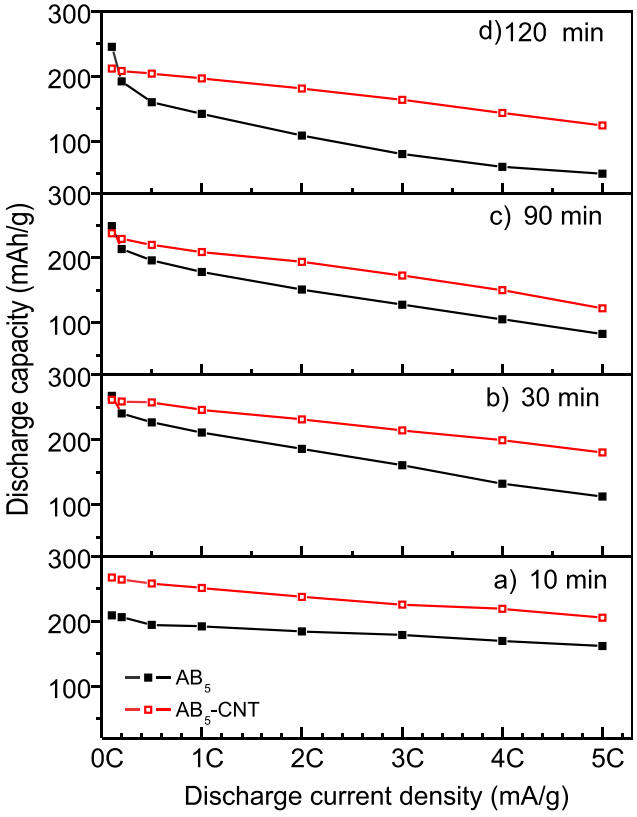

Fig. 6 – Rate capability of working electrode made with alloy and alloy-CNTs mechanically milled.

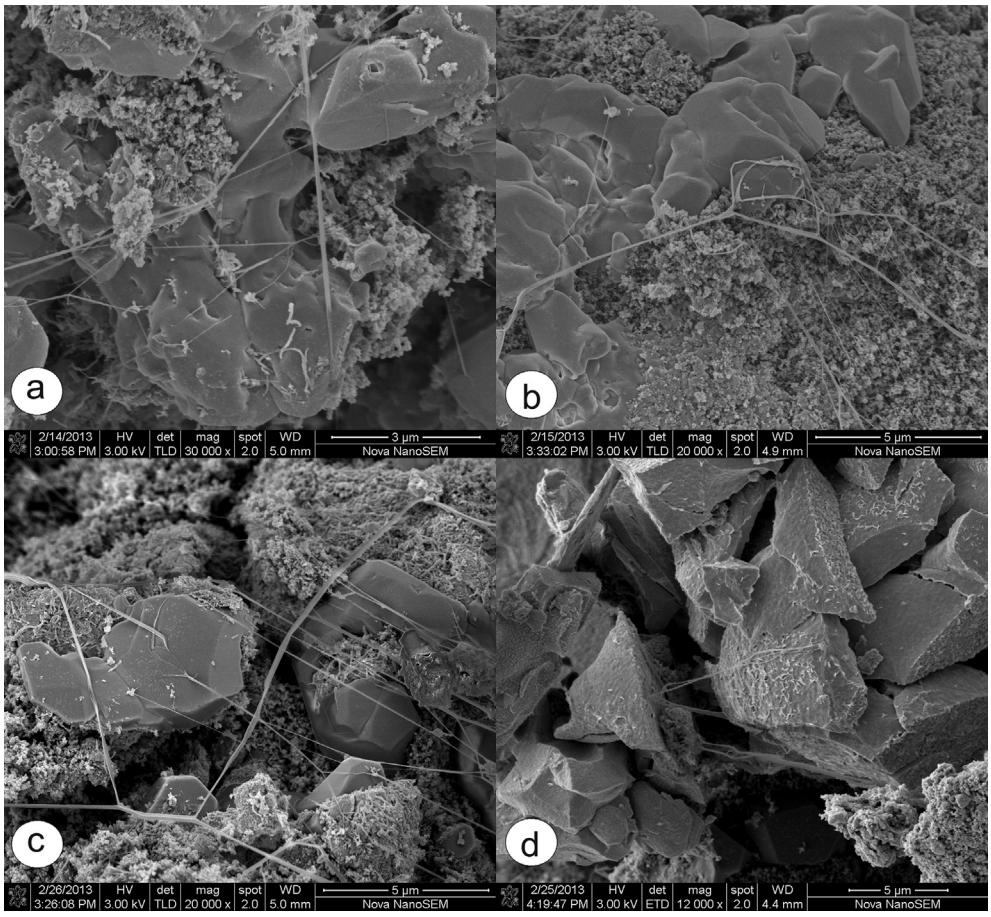

Fig. 7 – Working electrode made with alloy-CNTs a) 10 min, b) 30 min, c) 90 min y d) 120 min.

than 30 min the C_d at 0.1C rate of electrodes with single alloy are higher than the ones with CNTs-added.

The electrochemical results indicate that the electrodes made with the CNTs-added alloy show greater C_d. This may be due to the reduced stability of some interstitial sites caused by the defects created by mechanical alloying in the single milled alloy. It is also expected that the crystallite size reduction, increase the density of structural defects such as dislocations or grain boundaries. This effect can reduce the diffusion of protons and hence the overall electrochemical capacity [13].

The micrographs of the electrodes (Fig. 7) show the interaction of the alloy-nanotubes due to the mechanical milling process applied. The nanotubes are aligned and distributed throughout the electrode. Many of them seem to be encrusted or go through the alloy.

Conclusion

The nanotubes added to the mechanical milling of the alloy acted as a mechanical support preventing further decrease in crystallite size, as it occurred with the milling of the single alloy. These results are related to the retention of the electrochemical discharge capacity of the electrodes made with the CNTs-added alloy over the single alloy, 207 vs. 157 mAh/g at 120 min of milling. The grinding of alloy has a greater insertion of structural defects, which can produce samples with high internal stress, increasing the free energy of the material and carrying of the equilibrium pressure range used for the electrochemical studies, thus reducing the capacity.

Acknowledgements

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