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Research Article

Characteristics of the $Ti_{1.27}Fe$ + 11 wt.% Ni Composite Obtained by Arc Melting and Ball Milling

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The $Ti_{1.27}Fe$ + 11 wt.% Ni composite synthesized by arc melting and ball milling and its possible use in hydrogen storage were studied. First the intermetallic $Ti_{1.27}Fe$ was obtained from elemental powders of Ti and Fe by using the arc melting in argon atmosphere and was cracked in a reactor, after that nickel powder was added to the $Ti_{1.27}Fe$ alloy before the milling. The mixture was subjected to high-energy ball milling to produce the $Ti_{1.27}Fe$/Ni composite. Nanocrystalline phases $Ti_{1.27}Fe$ + Ni were observed after 5 h of milling. Hydrogenation results indicated that in the first cycle of hydriding the maximum amount of hydrogen release was 2.10 wt.% for the composite at 100°C, under hydrogen pressure of 0.8 MPa and without prior activation.

1. Introduction

The intermetallic compound TiFe is one of the most well-known alloys as a hydrogen storage material, because of abundance and low cost of raw material and moderate conditions for hydrogenation/dehydrogenation processes. However, it requires some activation treatments before hydrogen reaction, for example, heating over 400–450°C in vacuum and subsequent annealing in hydrogen at pressures of 0.7–1.0 MPa, followed by cooling to room temperature and exposure to hydrogen at pressures of 3.0–6.5 MPa. The activation processes of hydrogenation, charging-discharging, have to be repeated several times to obtain reproducible pressure-concentration isotherms [1–5]. To improve hydrogenation/dehydrogenation processes, several treatment have been reported with respect to the TiFe alloy composition, by substituting Fe in FeTi alloy for transition elements such as Ni, Mn, Zr, and others or by modifying the surface of the alloy via the induction of an specific oxide, such as NbO, Cr_2O_3 [6–11]. Currently, new development and research are focusing on obtaining metal matrix nanocomposites with outstanding microstructural properties, such as specific area, size grain, dislocations, and diameter pore. Recently, mechanical alloying (MA) and mechanical grinding (MG) have extensively been used to synthesize various nonequilibrium alloys, nanocomposites, amorphous and nanocrystalline materials. As it is known that modified nanocomposites are used as hydrogen storage materials, these alloys were also applied for the Ni-MH batteries. A large number of works on hydrogen absorption and activation properties for TiFe alloys produced by MA or MG have been reported [12–18].

The present work is related to the characteristics of the $Ti_{1.27}Fe$ + 11 wt.% Ni composite obtained by arc melting and ball milling process. The addition of nickel on TiFe alloy, improved the hydrogen absorption-desorption process, the difference in the hydrogen storage characteristics for this composite was correlated with its composition and microstructure.

2. Experimental Procedure

For the synthesis of TiFe alloy, a mixture (atom ratio 1.27 : 1) of Ti (98.0%, <325 mesh) and Fe (99.5%, <200 μm) was melting in an arc melting device under an argon atmosphere on a water-cooled Cu hearth. A button shape alloy was obtained, crushed and pulverized in a mortar of stainless steel, and ground into powder <115 mesh to obtain particles size less than 125 μm in diameter. To embrittle the alloy powder was immediately loaded into the reactor and thermaly treated at 350°C for 3 h under hydrogen pressure of 4 MPa. $Ti_{1.27}Fe$ + 11 wt.% Ni was then mechanically milled into a tungsten carbide vial together with stainless steel balls under argon atmosphere. The ball-to-powder weight ratio was 4 : 1. Process control agent of methanol was added to the powder mixture to prevent agglomeration and reaction with Ti. The milling was carried out for 5 h in argon atmosphere by using a high energy ball mill type Spex 8000 designed at Instituto Nacional de Investigaciones Nucleares [19].

The hydrogen absorption property of $Ti_{1.27}Fe$ + 11 wt.% Ni composite was evaluated in a 50 mL capacity stainless steel reactor, by exposing the powder sample to gaseous hydrogen (99.999% nominal purity). Prior to hydriding reaction, the ball-milled powder was vacuum-heated up to 100°C during 3 h. The hydrogen absorption of composite was carried out at temperature of 100°C under H_2 pressures between 0.2 and 1.4 MPa during 30 minutes.

Samples characterization, before and after hydrogen reaction, were carried out by X-ray diffraction (XRD) analysis on a Siemens D5000 diffractometer with Cu Kα radiation, scanning electron microscopy (SEM; Phillips XL30), and transmission electron microscopy (TEM; Jeol 2010 HT). Energy dispersive X-ray (EDS) analysis was used for elemental analysis of the selected microarea and inductively coupled plasma-optical emission spectroscopy (ICP) for elemental quantitative analysis. The surface area was determined from the nitrogen adsorption isotherm by the BET method and the pore size distribution from the branch desorption by the BJH method. Nitrogen adsorption of the milled samples was measured at −196°C with an equipment of physisorption, Belsorp Max Japan INC. Prior to the measurement, the samples were degassed at 150°C for 3 hours in nitrogen atmosphere. To evaluate the hydrogen content in the composite, it was analyzed by simultaneous differential technique (SDT), analyzer (DSC-TGA) before and after the hydrogenation process using Calorimeter TA Instruments-Waters model SDT Q600, previously calibrated.

3. Results and Discussion

3.1. Structure of Synthesized $Ti_{1.27}Fe$ + 11 wt.% Ni Composite. The XRD patterns of Ti-Fe/Ni mixture at various stages of the process are presented in Figure 1. X-ray diffraction pattern of initial powder mixture shows only Bragg reflections from elemental Ti and Fe, Figure 1(a). Figure 1(b) shows characteristics reflections of the formation of the phase TiFe during melting. Other peaks of small intensity were also identified that correspond to the TiFeO phase. Figure 1(c) corresponds to the XRD pattern of nickel powder, before being added and milling with the $Ti_{1.27}Fe$ alloy. After milling in an inert atmosphere for 5 h, the peaks of the TiFe pattern are broadened indicating the formation of a nanocrystalline cubic structure. Broadening of all the diffraction reflections and decrease in intensity of single TiFe phase with CsCl type structure suggest the existing of microstrains and/or small crystallite sizes in the existing crystalline phases. The *a* lattice parameter of $Ti_{1.27}Fe$ alloy after milling was 0.2972 nm for TiFe phase. This lattice parameter value is slightly small, with respect to the reference TiFe value of 0.2976 nm from JCPDS (Card no. 19-0636) [20]. The crystallite size of TiFe phase was estimated to be about 11 nm. It was calculated from the width of its XRD peaks, by using the Sherrer formula. Also reflections of nickel and TiFeO were observed as it is shown in Figure 1(d). As it can be noticed, pure Ni diffraction can be seen after 5 h milling, implying that nickel is only dispersed in the $Ti_{1.27}Fe$ alloy.

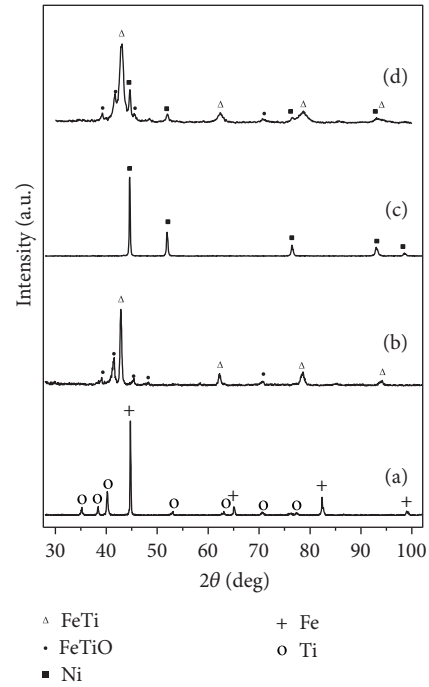

Figure 1: XRD profiles of Ti-Fe/Ni mixtures at different stages of processing: (a) elementary powders mixtures, (b) arc melting $Ti_{1.27}Fe$, (c) Ni powder, and (d) $Ti_{1.27}Fe$ + 11 wt.% Ni after 5 h of ball milling.

The nanocrystalline structure of the milled sample was verified by TEM observations. Figure 2(a) shows a dark-field TEM image from a powder particle of $Ti_{1.27}Fe$ + 11 wt.% Ni composite prepared by ball milling for 5 h. From the dark-field image, the crystallites of small size, about 12 nm, are clearly displayed in the dark-field imaging mode. Crystallite sizes are consistent with the X-ray diffraction estimation from broadening of the peaks. Selected area electron diffraction (SAD) pattern of composite powder after ball milling process is shown in Figure 2(b). SAD pattern exhibited diffraction rings for the (110), (200), and (211) this confirms that the composite has crystalline cubic structure that corresponds to the TiFe phase and this was according to XRD result.

Table 1: Composition $Ti_{1.27}Fe$ + 11 wt.% Ni composite analyzed by ICP-OES and EDS.

Sample	Ball milling (h)	Nominal composition (at. %)			ICP-OES composition (at. %)			EDS composition (at. %)		
		Ti	Fe	Ni	Ti	Fe	Ni	Ti	Fe	Ni
Composite	5	50.0	40.0	10.0	49.6	40.2	10.2	50.4	39.9	9.7

Table 2: Hydrogen absorption/desorption capacity for the $Ti_{1.27}Fe$ + 11 wt.% Ni composite as a function of the pressure.

Hydrogen process[a]	
Pressure (MPa)	Mass loss (wt.%)
0.2	1.562
0.4	1.662
0.6	1.789
0.8	2.107
1.0	1.579
1.2	1.398
1.4	1.387

[a]Hydrogenation conditions: $T = 100^{\circ}C$, $t = 30$ min.

The SEM images of $Ti_{1.27}Fe$ alloy, $Ti_{1.27}Fe$ + 11 wt.% Ni composite and hydrogenated composite, are shown in Figures 3(a)–3(d). The average particle size of $Ti_{1.27}Fe$ alloy obtained by arc melting crushed and pulverized in a mortar of stainless steel is about 125 μm in diameter as it is observed in Figure 3(a). Morphology of the same sample is shown in Figure 3(b). A dendritic structure and homogeneous morphology were observed for the melted alloy that is typical for powder of brittle metallic materials. After 5 h of milling of $Ti_{1.27}Fe$ + Ni mixture, Figure 3(c), a great reduction in particle size less than 4 μm is observed. Thus the fracture and fragmentation of $Ti_{1.27}Fe$/Ni during ball milling decrease drastically the particle size. Furthermore SEM showed that nickel is completely dispersed in $Ti_{1.27}Fe$ alloy. The dispersion of nickel in the $Ti_{1.27}Fe$ alloy during the milling could accelerate the hydrogen absorption kinetics. The image of Figure 3(d) corresponds to the hydrogenated composite, heated at 100°C under hydrogen pressure of 0.8 MPa. It is observed that morphology of the particles is sponged and tends to disaggregate into fine particles due to the interaction with hydrogen.

ICP-OES and EDS chemical composition of $Ti_{1.27}Fe$ + 11 wt.% Ni composite with 5 h of milling is shown in Table 1. Results show that the deviation of Ti-Fe-Ni ratio from nominal composition was negligible. It must be said that oxygen is not detected by ICP-OES; however, oxygen was found in the composite by EDS, which corresponds to the TiFeO as mentioned in XRD Figures 1(b) and 1(d).

According to the BET method, the $Ti_{1.27}Fe$ + 11 wt.% Ni composite has a surface area of 3.2073 m^2/g. Thus the fracture and fragmentation of composite powders during ball milling increase drastically the surface area. The pore size distribution of the mesoporous composite was calculated from adsorption branch of the isotherm by the BJH method. An average pore radium of 12.1 Å has found total specific pore volume (P/P_o) of 0.022912 cm^3/g.

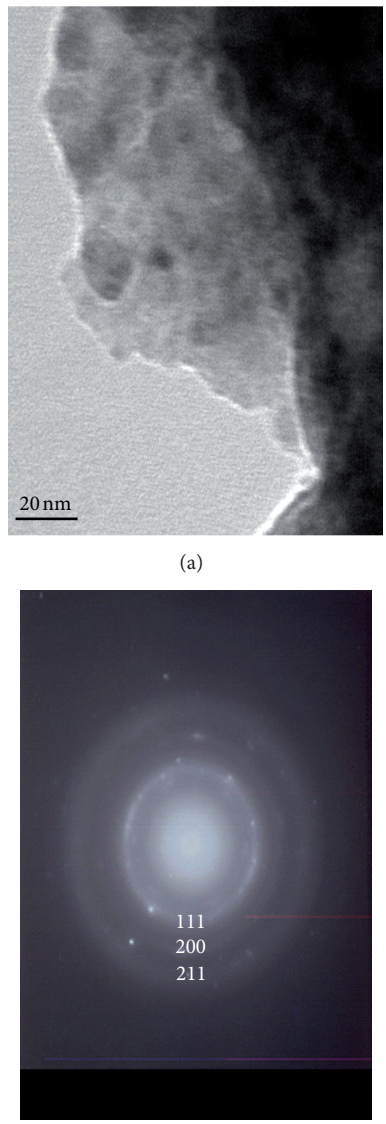

Figure 2: TEM images of $Ti_{1.27}Fe$ + 11 wt.% Ni composite after 5 h of ball milling: (a) dark-field image and (b) selected-area electron diffraction patterns.

3.2. Hydrogenation Properties. Hydrogenation properties for the $Ti_{1.27}Fe$ + 11 wt.% Ni composite obtained for 5 h milling at 100°C are in Figure 4 and Table 2. Hydrogenation process for 0.5 h at 100°C and pressures of 0.6–1.8 MPa and only one cycle were tested. Composite sample was activated by heat treatment at 100°C in vacuuming and 1.33 Pa in hydrogen atmosphere for 3 h prior to hydrogenation process. As can be noted the maximum capacity absorption/desorption of hydrogen for the composite was 2.107 wt.% at 100°C and

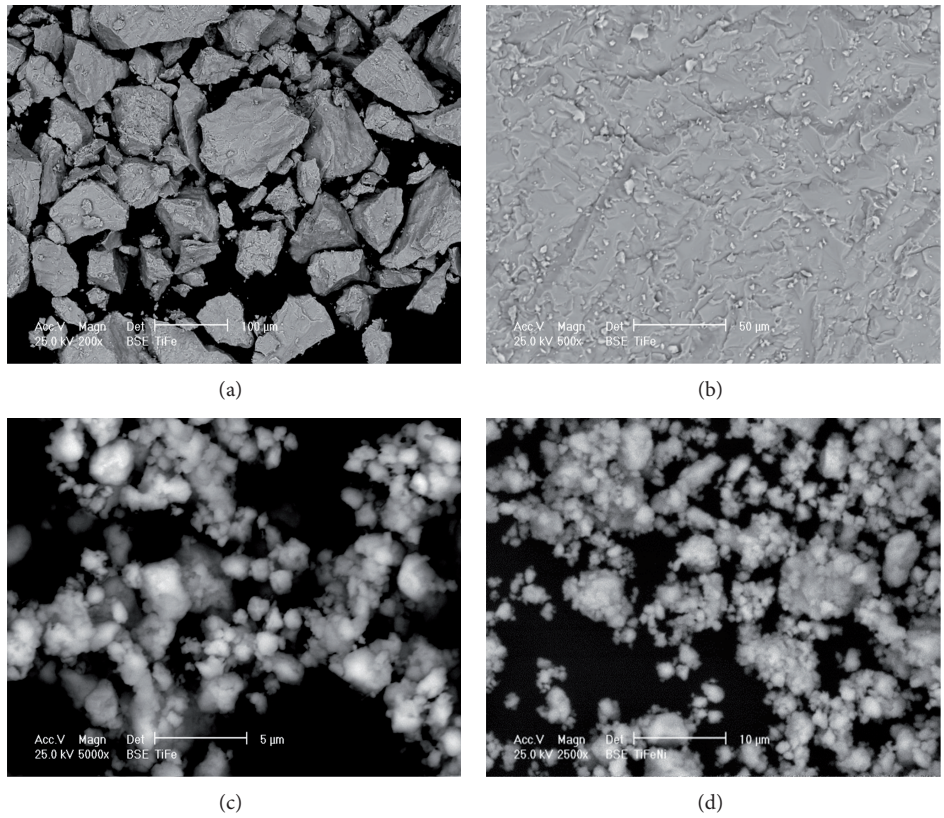

Figure 3: SEM micrographs of $Ti_{1.27}Fe$/Ni at different stages of processing: (a) $Ti_{1.27}Fe$ alloy-as melted, (b) homogenized, (c) TiFe + 11 wt.% Ni after 5 h of ball milling, and (d) hydrogenated composite.

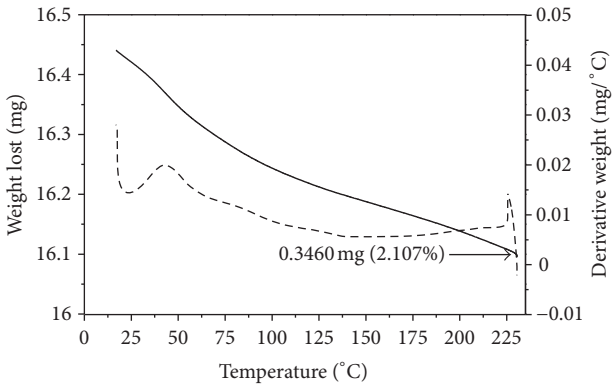

Figure 4: TGA profile (—) and its derivative (- - -) of hydrogenated $Ti_{1.27}Fe$ + 11 wt.% Ni composite indicating wt.% H_2 released as function of the temperature.

a pressure of 0.8 MPa; however, this capacity decreased at higher pressures, which means that the system has reached its saturation pressure starting to release hydrogen by pressure effect.

4. Conclusions

In this work, we have successfully obtained the $Ti_{1.27}Fe$ + 11 wt.% Ni composite by arc melting and ball milling in a short period of time. The process of embrittlement at 350°C and 4 MPa in hydrogen atmosphere of the $Ti_{1.27}Fe$ alloy obtained by arc melting facilitates the obtaining of composite of $Ti_{1.27}Fe$ + 11 wt.% Ni by ball milling in a time of 5 h. A nanocrystalline TiFe single phase of CsCl-type structure has been observed after 5 h of milling. The obtained composite is enough close with its theoretical composition. The produced composite by ball milling is able to absorb hydrogen at 100°C and low pressures in 0.5 h. The surface area and crystallite size improve the capacity of hydrogen absorption. The presence of Ni in the $Ti_{1.27}Fe$ alloy enhances its catalytic activity for the hydrogenation process without prior activation.

Future research is aimed to investigate the entire process of hydrogenation/dehydrogenation of this composite.

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