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Unconventional synthesis of $Mg_xC_yNi_3$: Synergic combination of mechanical alloying, SHS and isothermal heating

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Several methods have been tested in order to prepare the perovskite type compound $Mg_xC_yNi_3$ applying the mechanical alloying (MA), the self-propagating high-temperature synthesis (SHS) and the isothermal heating techniques in the different steps of preparation. These methods may be summarized as follows: *method MCN-1*) synthesis of the $Mg_xC_yNi_3$ phase through MA of Mg_2Ni (previously synthesised by isothermal heating) and selected amounts of graphite and Ni, followed by isothermal treatment; *method MCN-2*) synthesis of the $Mg_xC_yNi_3$ phase applying the SHS technique using powder compacts; *method MCN-3*) synthesis of an eutectic sample composed of Ni and $MgNi_2$ by means of isothermal heating, subsequent MA with graphite and final synthesis of $Mg_xC_yNi_3$ by means of SHS.

The methods MCN-2 and MCN-3 proved their validity to the synthesis of the desired compound with two main important results: complete conversion of the reactants into $Mg_xC_yNi_3$ and control of the stoichiometry in the final product. For instance method MCN-1 shows instead a very low degree of conversion of the reactants.

All the phases obtained after each preparation step (MA, SHS, isothermal heating) have been characterized by means of X-ray powder diffraction (XRPD), scanning electron microscopy (SEM) coupled with electron dispersive spectroscopy (EDS).

1. Introduction

Mechanical alloying (MA) [1] and self-propagating high-temperature synthesis (SHS), related to the combustion synthesis technique [2, 3], provide attractive alternative to the conventional methods for the synthesis of ceramics and intermetallic compounds. Both methods allow the preparation of a variety of equilibrium and non-equilibrium phases, starting from pure elements or pre-reacted precursors. In particular many reactions occurring during ball milling are similar to the SHS reactions and are mildly exothermic. As a consequence in many cases MA results coupled with SHS and as a result temperature increase is observed as well as metastable product formation. On the other hand in some cases the ignition of SHS is easier obtained after MA of the reactant powder mixture. In fact during MA two competitive mechanisms occur: (1) formation of a product that reduces the contact surface between the reactants, retarding the SHS ignition; (2) increase of the reactant particles mixing, resulting in a finer microstructure as ball milling proceeds that facilitates the ignition of SHS; in addition the defects introduced during MA in the crystal structure of the reactants may result advantageous in the ignition and sustaining of low exothermic reactions. One of the most important parameters in the SHS reactions is the reactant particle size, controlling the green density, the green pore size, the thermal conductivity of reactants and products and, in some cases, the reaction mechanism. An increase of the particle sizes can decrease the maximum combustion temperature, as well as the velocity of the propagation of the reaction front and hence also the degree of completion of the SHS reaction. For these reasons MA carried out before SHS may strongly influence its success, as well as the nature and the properties of the final products.

Mg-based alloys, primarily those containing Ni, are considered to be promising materials among the hydrogen storage materials for their high hydrogen storage capacity, light weight and low cost. These alloys are usually prepared by isothermal heating but, in this case, they have slow hydriding and de-hydriding kinetics. In

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fact the Mg—H bond is very stable and a relatively high amount of energy is needed for its breaking. Alloying Mg with other elements could lower the stability of the hydride without decreasing the storage capability. Mechanically alloyed mixtures show higher hydriding and de-hydriding rates. Some further improvements have been recently observed in Mg—Ni—C composites when nanoparticle forms are obtained by ball-milling of graphitic carbon.

The formation of a nanocrystaline or amorphous phase and the modification with another material by MA may lead to an improvement in their hydriding/dehydriding and/or charge/discharge characteristics. In fact, recently it has been shown that the MA can be utilised for the synthesis of hydrogen storage materials such as $Ni_{60}Ti_{40}$ [4] and Mg_2Ni [5, 6]. Different alloying elements were also used to improve the hydrogen adsorption/desorption properties [7–11] Nohara *et al.* [12] investigated the effect of the surface modification by ball milling on the rate of hydrogen adsorption of a Mg-Ni alloys with C: MA was found to be extremely effective for increasing the rate of hydrogen adsorption without decreasing the capability of storage. In addition ball-milled C was found to adsorb hydrogen more efficiently when mixed with Ni [13].

In this work different methods for the synthesis of $Mg_xC_yNi_3$ are tested, in order to explore its capability as hydrogen storage material in the future; these methods result from the combination of different preparation techniques: MA, SHS and isothermal heating.

2. Experimental

The mechanical alloying was carried out by means of a Fritsch Pulverisette 5 planetary ball-mill with an acceleration of ca. 100 m/s^2 for selected periods in a stainless steel vial under Ar atmosphere, using hardened Cr-steel milling tools and an initial ball-to-powder weight ratio equal to about 5:1. The combustion reactions were ignited by means of a Joule heated W-coil at the top of cylindrical powder compacts of the reactants under an Ar atmosphere. The preparation methods investigated in this work may be schematically summarized as follows:

- *method MCN-1*: (1) synthesis of Mg_2Ni by isothermal heating; (2) MA (1st step: 120 rpm, 24 h; 2nd step: 180 rpm, 168 h) of stoichiometric powder mixture of Mg_2Ni, C and Ni; (3) isothermal heating of the powder compact at 673 K for 168 h under vacuum;
- *method MCN-2*: (1) SHS of a powder compact with an almost stoichiometric composition (Mg in slight excess); (2) isothermal heating of the powder compact at 1123 K for 134 h under Ar;
- *method MCN-3*: (1) synthesis of a sample with eutectic composition Ni and $MgNi_2$ (molar ratio 1:1) by isothermal heating; (2) MA with stoichiometric amounts of C (180 rpm for 200 h); (3) SHS of the powder compact under Ar.

After each step of reaction (MA, SHS, isothermal treatment) the products were characterised by means of X-ray powder diffraction analysis (XRPD: Philips PW1830; Bragg-Brentano geometry; Cu K_α; secondary monochromator; 2θ range 20–80; step 0.05 2θ; sampling time 3 s), scanning electron microscopy observation (SEM: Cambridge S360) in back-scattered electron (BSE) and secondary electron (SE) modes coupled with electron dispersive spectrometer chemical analysis (EDS: Oxford Link Pentafet).

3. Results and discussion

3.1. Method MCN-1

XRPD analysis performed after the first treatment of MA carried out at 120 rpm for 24 h in Ar reveals the presence of C, Mg_2Ni, and Ni (Fig. 1a). After this step, several MA treatments followed at 180 rpm, for a total time of further 168 h. Both C and Mg_2Ni undergo a strong amorphization as MA proceeds, whereas the amount of defects content in Ni increases, as revealed by the increase of lines broadening measured as full width at half maximum (FWHM) (Fig. 1b). No evidence for the formation of new phases may be detected. Fig. 2 shows the evolution of the sample powders after MA at 120 rpm for 24 h (Fig. 2a) and a subsequent treatment at 180 rpm for further 24 h (Fig. 2b).

The final isothermal treatment leads to the recrystallization of Ni and the incipient growth of a minimum amount of $Mg_xC_yNi_3$, revealed by a faint peak in the XRPD pattern (Fig. 1c).

From the above results it may be concluded that $Mg_xC_yNi_3$ may not be prepared directly by MA of the precursor Mg_2Ni with stoichiometric amounts of

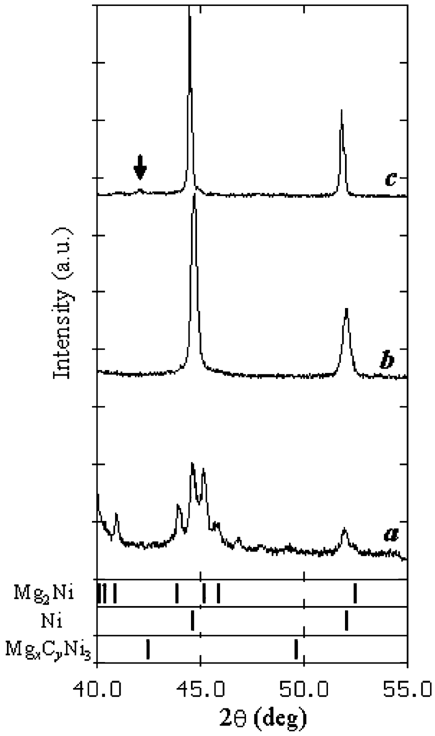

Figure 1 Selected portions of XRPD patterns collected at different steps of preparation of $Mg_xC_yNi_3$ applying the method MCN-1: (a) after 24 h of MA, (b) after 192 h of MA, and (c) after the final isothermal treatment: a faint peak due to $Mg_xC_yNi_3$ may be distinguished (arrowed).

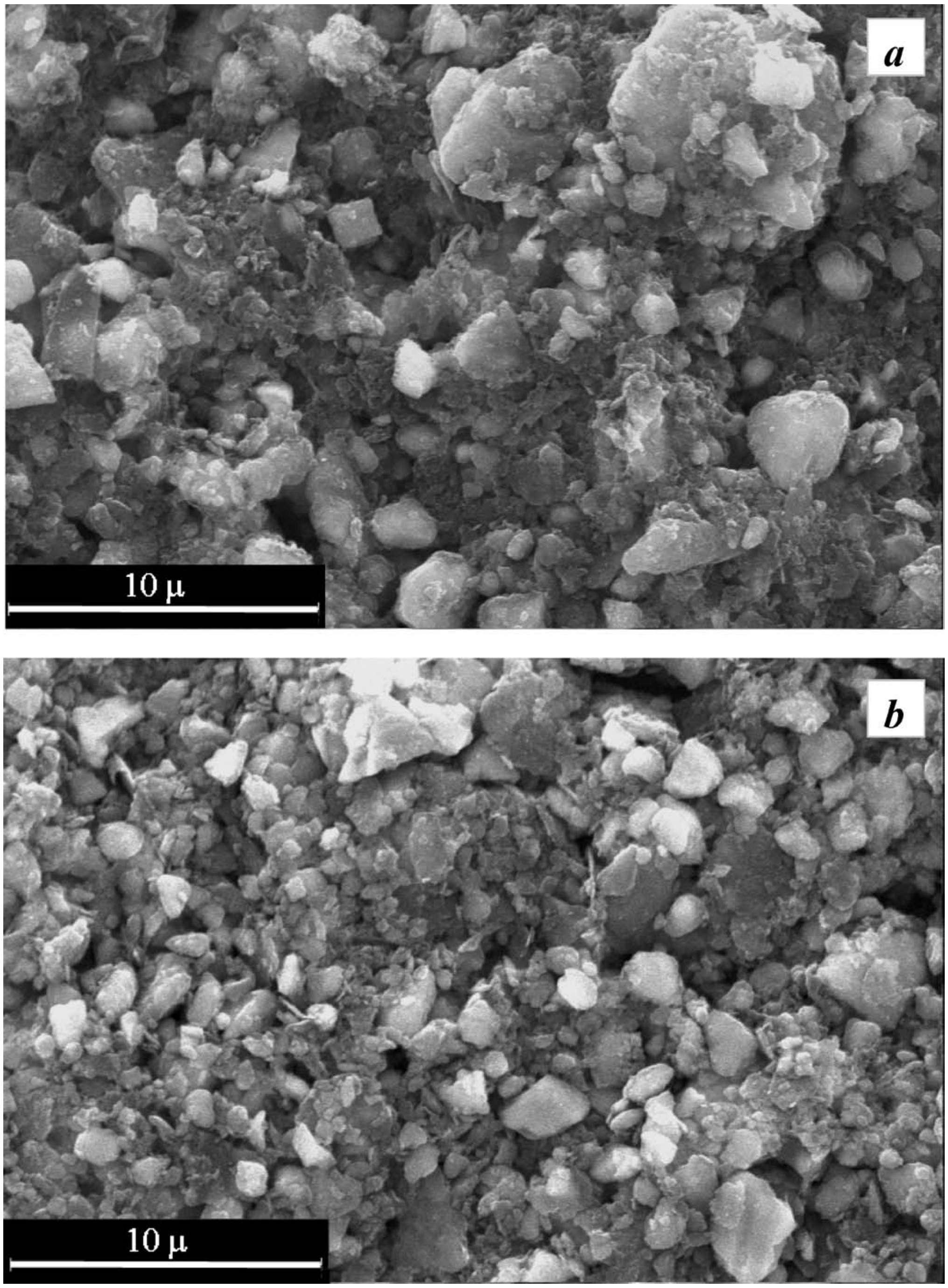

Figure 2 Method MCN-1: evolution of the sample powders after MA at 120 rpm for 24 h (a) and the subsequent treatment at 180 rpm for 24 h (b).

Ni and C; only after equilibration very few amounts of perovskite may be obtained.

3.2. Method MCN-2

XRPD analysis performed after the SHS reaction reveals the incipient formation of $Mg_xC_yNi_3$, although the sample is mainly composed of pure Ni and two different phases whose structures and compositions (as evidenced by EDS analyses) are strongly related to Mg_2Ni and $MgNi_2$, respectively. The pellet was hence hand milled and a new powder compact was prepared and equilibrated at 1123 K under an Ar atmosphere. At the end of the preparation the sample shows a light grey colour with metallic lustre. XRPD analysis reveals the almost complete conversion of the starting elements into the perovskite (Fig. 3); faint peaks of $MgCO_3$ may be distinguished: this phase forms because of the strong Mg excess used in the starting reactant mixture in order to prevent the eventual Mg loss due to its volatilization. On the other hand $MgCO_3$ may be easily distinguished using a low magnification optical microscope as sub-millimetric white and almost transparent crystals; in addition no evidence for unreacted C may be detected. SEM observation does not evidences the presence of other secondary phases (Fig. 4); the nominal composition of the perovskite as obtained from the EDS data may be referred to as $Mg_{1.29}C_{1.00}Ni_3$. In conclusion the application of this method leads to two main important results: (1) almost complete conversion of the reactants into $Mg_xC_yNi_3$; (2) control of the stoichiometry of the final products, since no Mg loss may

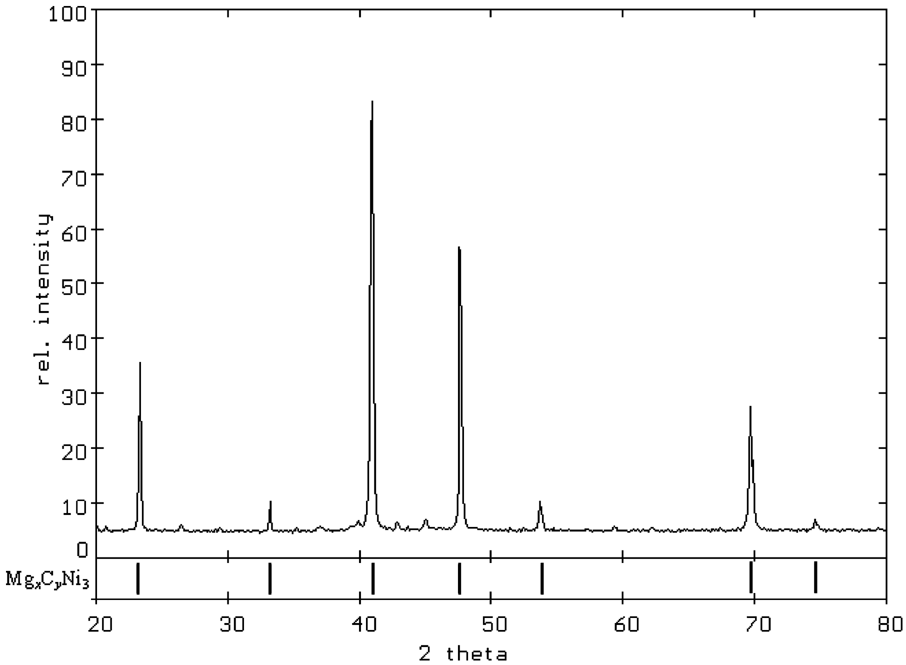

Figure 3 XRPD pattern of $Mg_xC_yNi_3$ as obtained by means of method MCN-2.

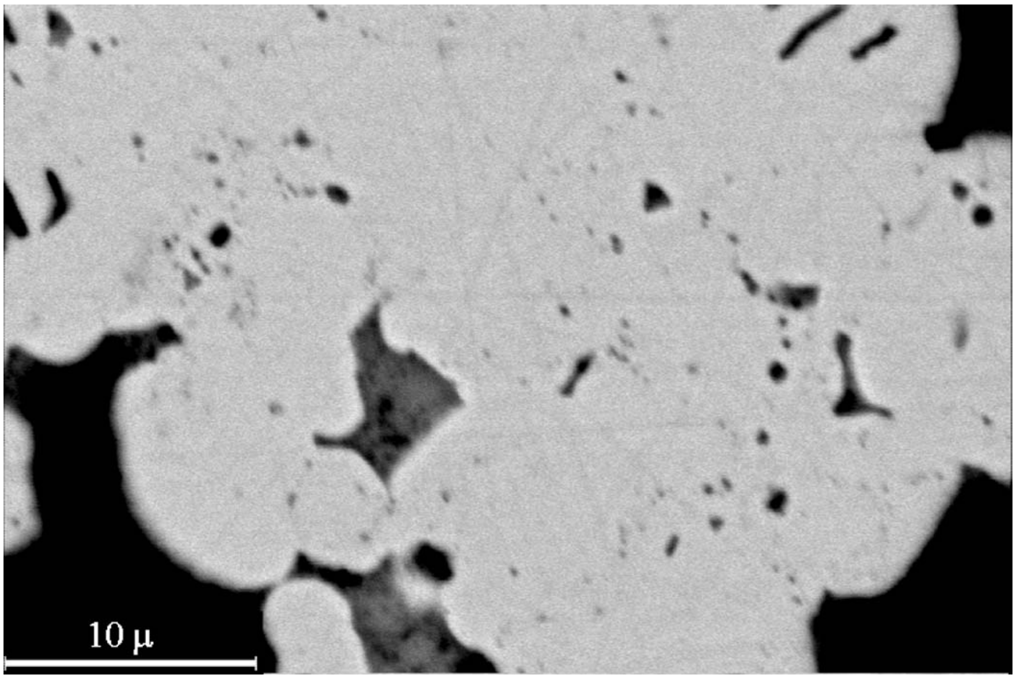

Figure 4 BSE image of $Mg_xC_yNi_3$ obtained applying the method MCN-2; no evidence for dispersed secondary phases may be detected.

be detected. Due to the goodness of the obtained results this method has been investigated more in detail [14].

3.3. Method MCN-3

Line broadenings in the XRPD patterns reveal an increases of the defects content as the MA proceeds on the powder mixture composed of C and the two-phase sample (Ni + $MgNi_2$) (Fig. 5a and b). The SHS reaction was easily ignited on the compact composed of this activated powder mixture; after reaction the XRPD pattern reveals the complete conversion of the reactants into $Mg_xC_yNi_3$ (Fig. 5c); no evidence for the presence of secondary phases may be detected. In this case the importance of the MA treatment of the reactant powders is dramatically evidenced: compared to the method MCN-2 where after SHS of unmilled particles very few amounts of perovskite are obtained, in this case a massive transformation of the reactants into $Mg_xC_yNi_3$ is obtained, thanks to the preliminary MA treatment that increases the reactant powder mixing and their content of lattice defects.

In conclusion the MA of the reactant particles strongly influences the SHS process, since the reactants are completely converted into the desired product and further thermal treatments are no more needed; in addition also this method proved its validity for the

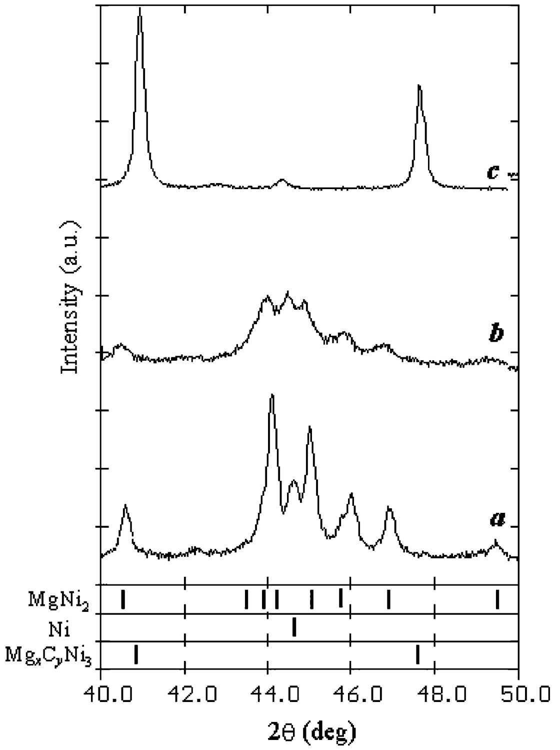

Figure 5 Selected portions of XRPD patterns collected at different steps of preparation of $Mg_xC_yNi_3$ applying the method MCN-3: (a) after 100 h of MA, (b) after 200 h of MA, and (c) after the final SHS treatment evidencing the almost complete conversion of the reactants into $Mg_xC_yNi_3$.

preparation of $Mg_xC_yNi_3$ with controlled stoichiometry, at least for what concerns the [Mg]/[Ni] ratio.

4. Conclusions

Several methods for the synthesis of the perovskite-type compound $Mg_xC_yNi_3$ have been tested, by synergetic combination of MA, SHS and isothermal treatment. MA has proved its importance on the evolution of the SHS reaction, increasing the defects content of the reactants and activating the low exothermic reactions that lead to the formation of the desired product; as a result ball-milled particles may be completely converted into $Mg_xC_yNi_3$ during SHS. On the contrary a minimal amount of perovskite forms during the SHS of un-milled reactants and an high temperature isothermal treatment is needed to transform the so obtained products into the desired product. As a consequence MA of the reactant powder mixture can control the degree of completion of the SHS reaction. On the other hand the unique MA treatment does not lead to the formation of $Mg_xC_yNi_3$ as well as any other phase in detectable amount. In conclusion methods MCN-2 and MCN-3 proved their validity to the synthesis of the desired compound with two main important results: complete conversion of the reactants into $Mg_xC_yNi_3$ and control of the stoichiometry in the final product. For instance method MCN-1 shows instead a very low degree of conversion of the reactants.

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References

1. C. SURYANARAYANA, *Progr. Mater. Sci.* **46** (2001) 1.
2. J. J. MOORE and H. J. FENG, *ibid.* **39** (1995) 243.
3. *Idem., ibid.* **39** (1995) 275.
4. J. C. DE LIMA, D. M. TRICHES, T. A. GRANDI and R. S. DE BIASI, *J. Non-Cryst. Solids* **304** (2002) 174.
5. S. S. HAN, H. Y. LEE, N. H. GOO, W. T. JEONG and K. S. LEE, *J. Alloys Compd.* **330–332** (2002) 841.
6. T. SPASSOV, P. SOLSONA, S. SURINACH and M. D. BARO, *ibid.* **349** (2003) 242.
7. D. S. DOS SANTOS, M. BOUOUDINA and D. FRACHART, *Int. J. Hydr. En.* **28** (2003) 1237.
8. M. Y. SONG, J.-P. MANAUD and B. DARRIET, *J. Alloys Compd.* **282** (1999) 243.
9. K. TANAKA, Y. KANDA, M. FURUHASHI, K. SAITO, K. KURODA and H. SAKA, *ibid.* **293–295** (1999) 521.
10. A. GASIOROWSKI, W. IWASIECZKO, D. SKORYNA, H. DRULIS and M. JURCZYK, *ibid.*, in press.
11. W. LIU, H. WU, Y. LEI, Q. WANG and J. WU, *ibid.* **261** (1997) 289.
12. S. NOHARA, H. INOUE, Y. FUKOMOTO and C. IWAKURA, *ibid.* **252** (1997) L16.
13. K. AWASTHI, R. KAMALAKARAN, A. K. SINGH and O. N. SRIVASTAVA, *Int. J. Hydr. En.* **27** (2002) 425.
14. M. FERRETTI, C. CICCARELLI, E. MAGNONE, S. RUBINO, N. PARODI and A. MARTINELLI, *Mater. Res. Bull.* **39** (2004) 647.

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