

Synthesis of NiMn_2O_4 assisted by high-energy ball milling of NiO - MnO powders

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This work presents a useful example of the fact that mechanical activation promotes solid state reaction in the preparation of a NiMn_2O_4 from NiO and MnO ; shown evidence demonstrates that high-energy ball milling of MnO and NiO powders followed by a heat treatment can be considered a possible route for the synthesis of this compound. The powders were milled at room temperature in a shaker mixer in a weight ratio 1 : 10 of powder to zirconia balls. X-ray diffraction patterns show small differences among the powders milled for different times, while post milling heat treatments conducted at different temperatures for 1 hour showed an increase in the formation of the nickel spinel with a tetragonal structure, which was successfully obtained with this combined mechanosynthesis (MSP) - heat treatment method.

Key words: Spinel, Nickel manganite, Ball milling, Mechanosynthesis.

Introduction

Nickel-manganese spinels are ceramic oxides often doped with 2+ metallic cations, such as Fe, Co, Cu and La for applications in electronics in devices such as thermistors of negative temperature coefficient resistance (NTC) [1, 2]. They are usually produced by chemical synthesis through soft chemistry followed by a sintering process which provides stoichiometric homogeneity and a narrow particle size distribution [3].

Mechanosynthesis processing (MSP) is a method based on mechanical activation of chemical reactions by high energy milling [4-6], which has been successfully applied to obtain different ceramic materials [7-9] and even other materials reported as very difficult to process such as Perovskites $\text{ErMn}_{1-x}\text{Ni}_x\text{O}_3$ [10].

The purpose of this study is to synthesize NiMn_2O_4 by high-energy ball milling of MnO and NiO powders followed by a heat treatment, proving that mechanical work is indeed an aid in the process by comparing the products obtained after different milling times and heat treatment temperatures.

Synthesis by a solid state reaction implies a high temperature in order to activate diffusion of matter; however this involves grain growth which is often against the properties for electronic applications. A combination of MSP and heat treatment consists in a simple process, which is MSP, that can be easily controlled, and the thermal one that thanks to the activation provided by the mechanical working can be performed either at a lower temperature

or a shorter processing time. In this research, the time of heat treatment is intentionally short in order to have incomplete reactions and then extract information that is useful to identify the contribution of MSP.

Experimental

Selected powders employed in this study where: MnO (ICSD 30520) and NiO (ICSD 87108), both from Sigma-Aldrich of 99.9% purity. Scanning electron microscopy (SEM) image of the MnO powders, about 100 μm in diameter is shown in Fig. 1, while NiO powders are between 5 μm and 10 μm in diameter, a few of them are even smaller (Fig. 2). X-rays mapping, also shown in the same figures confirms that the particles are indeed made of these compounds. The first step consisted in mixing these powders manually in a 0.45 NiO : 2.55 MnO ratio considering the wide range of oxides composition (Fig. 3) that could be formed.

Samples of 4 g of the powder mixtures, as well as six 12.7 mm diameter zirconia balls were loaded into cylindrical zirconia vials (60 cm^3). MSP was carried out at room

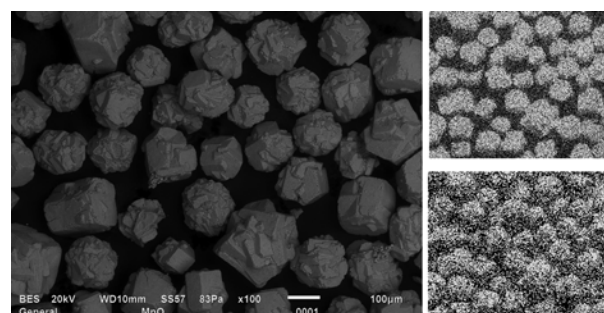


Fig. 1. Manganese oxide powder. Mn and O; X rays mappings are respectively shown above right and below.

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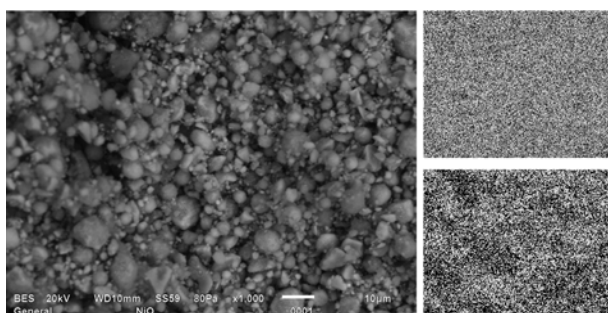


Fig. 2. Nickel oxide powders. Ni and O; X rays mappings are shown respectively above right and below.

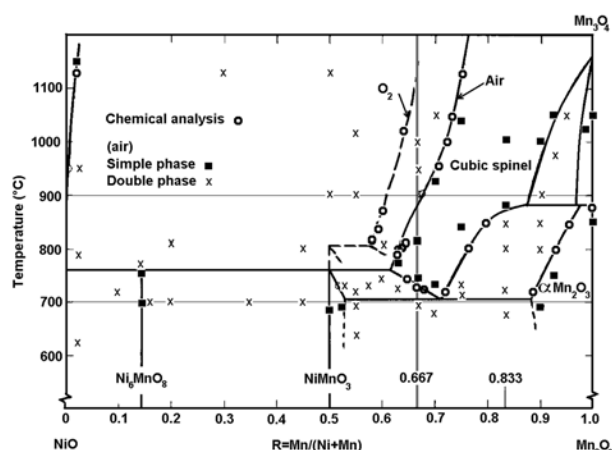


Fig. 3. Phase diagram of NiO-Mn₂O₃ system [11].

temperature by means of an SPEX 8000 D shaker mixer/mill. The powder-to-ball weight ratio was 1 : 10, while milling times were chosen inspired by previous research [4] as 1, 3, 5, 7 and 9 hours.

One hour thermal treatment at three different temperatures (500 °C, 700 °C and 900 °C) was conducted on all the samples after the milling process, including those that were only mixed manually. Given that the heat treatment time is the same for all the cases, differences among the products as a function of the milling time are useful for evidencing that the mechanical work energy is being stored, at least partially, by the powder system. A low temperature (500 °C) is known to be insufficient for producing synthesis in the solid state in 1 hour in air, and it is appropriated for actually detecting any improvement due to MSP. The upper temperature, 900 °C, which is enough for synthesis and sintering, but it is slightly in a wide range of compositions where either a spinel or a mixture of a spinel and NiO are stable, the products formed at this temperature will be indicators of the reaction path. An intermediate temperature (700 °C) was also chosen in order to detect MSP effects; this temperature is also an interesting because according to the equilibrium diagram shown in Fig. 3, it is around the eutectoid temperature. More about the chosen temperatures will be explained and considered in the discussion section. A short heat treatment allows the process to be followed and elucidates if MSP is actually

affecting the reaction of synthesis.

Track of the phase transformations as a function of the milling time was performed by means of X-ray diffraction patterns obtained at room temperature using a Philips X'Pert diffractometer. Diffraction patterns were collected in the range 10-70° (2θ) with increments of 0.02° (2θ) and counting time of 0.2 s per step. Cu-Kα (λ = 1.5418 Å) radiation was used in all experiments.

Results and Discussion

EDX analysis did not show evidence of any Zr, and then the only elements present are Mn, Ni and O. Fig. 4 shows the XRD of the mixtures milled at different times without heat treatment. Each pattern is shifted 200 counts up for clarity purposes. In a general sense it can be seen that as the milling time increases the peaks related to NiO decrease suggesting that this oxide is reacting to form another product. In Fig. 5 there is a closer view following an analysis as by Ashcroft *et al.* [12], where it is also noticeable that the MnO peak is decreasing as the milling time is increased. There are several NiO-MnO relationships within the cubic spinel region (Fig. 3) with peaks close to

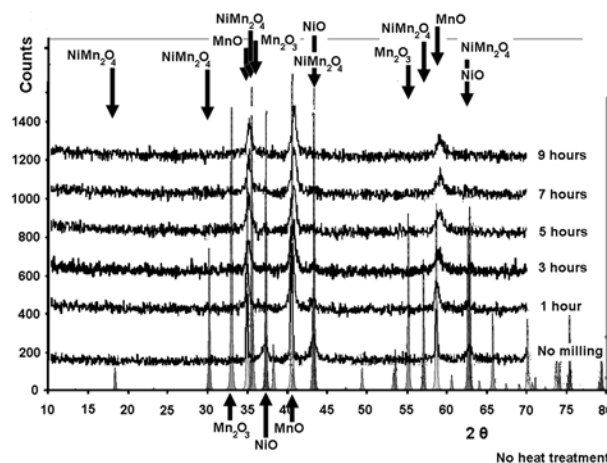


Fig. 4. X-rays powder diffraction patterns of mixtures of MnO and NiO milled into a zirconia vial for different times.

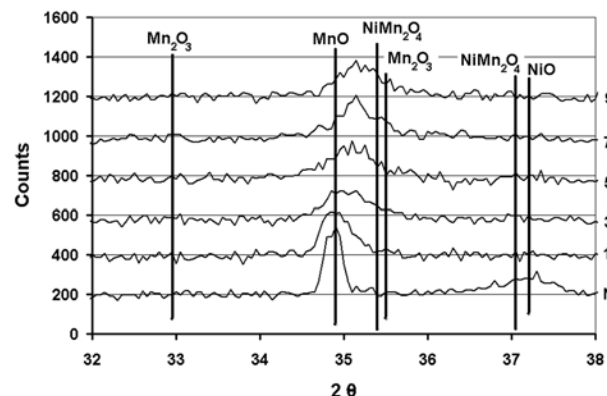


Fig. 5. Section between 32° and 38° of the X-rays powder diffraction patterns of the mixtures of Fig. 4.

those of the NiMn_2O_4 lattice that are overlapped explaining the shift of the peaks. There are other peaks out of the 32° to 38° frame, but the most evident are there.

An easier way for observing the effect of MSP is presented in Fig. 6, it is a radar chart with NiO , NiMn_2O_4 , MnO and Mn_2O_3 which are the main compounds identified. It is important to take into account that the points plotted do not correspond to the amount of each compound directly. This plot was built up by measuring the main peak of each compound in all the diffraction patterns obtained for the characterization of the samples. The maximum value was taken as 100% for each compound, and then the correspondent peak height was plotted in every chart in order to have the same scale. This method allows comparisons to be made given that all the diffraction patterns were obtained under the same conditions and although there could be some random variations the trend is the most important matter. Fig. 6 shows clearly that MSP is actually having an effect since the mixtures not milled are only NiO and MnO which are the raw materials, and then for longer milling times this changes as shown in the figure.

Gibbs free energy shows a greater stability of MnO over NiO , as can be seen in Fig. 7 [13, 14], therefore decomposition of NiO requires less energy. The atomic radii,

Mn^{2+} (0.80 Å) is larger than Ni^{2+} (0.69 Å) giving a direct idea of steric impediments, assuming that it is easier to introduce Ni^{2+} into the MnO lattice, rather than Mn^{2+} into the NiO structure. However this asseveration must not be taken as a law because there are reports showing that some large atoms diffuse faster than small ones [15]. Studies conducted by Franke and Dickmann [16] over diffusion of ^{59}Fe in a ferrite (Fe , Mn)O found diffusion coefficients of $10^{-7} \text{ cm}^2/\text{s}$ at 1000°C , while Peterson *et al.* [17] found diffusion coefficients of ^{59}Fe in magnetite (Fe_3O_4) of $10^{-9} \text{ cm}^2/\text{s}$ at the same temperature and in MnO it is $7.29 \times 10^{-8} \text{ cm}^2/\text{s}$ at 1007°C [18]. Assuming that Ni is similar to Fe , then its diffusion coefficient is greater than the diffusion coefficient of Mn in MnO , which has been reported as $2.01 \times 10^{-10} \text{ cm}^2/\text{s}$ at 997°C [19]. Similarities among the MnO - NiO compound lattices and the above statements allowing Ni^{2+} diffusion justify the disappearance of the peaks corresponding to NiO .

Fig. 8 shows details of the powder diffraction patterns of powder samples milled for different times and heat treated for one hour at 500°C . Peaks corresponding to NiO are not observed after 3 hours heat treatment. Peaks of NiMn_2O_4 (ICSD 9403) are not clear yet, but the ones from Mn_2O_3 (ICSD 33647) are stronger. This compound can be taken as evidence of energy stored by the system, and a process occurring out of equilibrium conditions [20].

Fig. 9 shows the radar chart where it is noticeable by

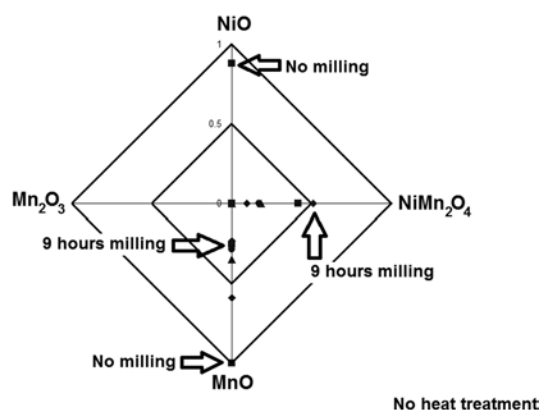


Fig. 6. Radar chart from the X-rays diffraction patterns shown in Fig. 5.

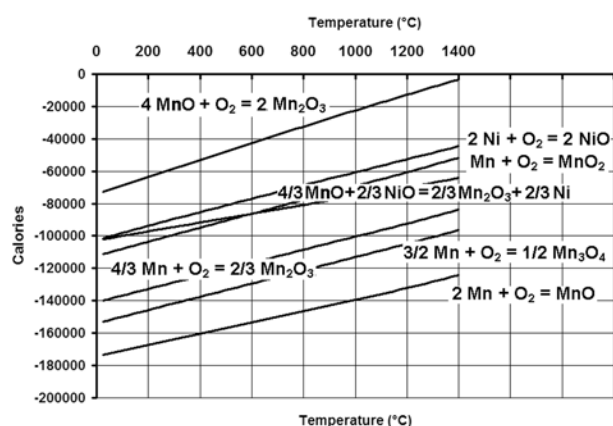


Fig. 7. Gibbs free energy diagram for several reactions at 1 atmosphere.

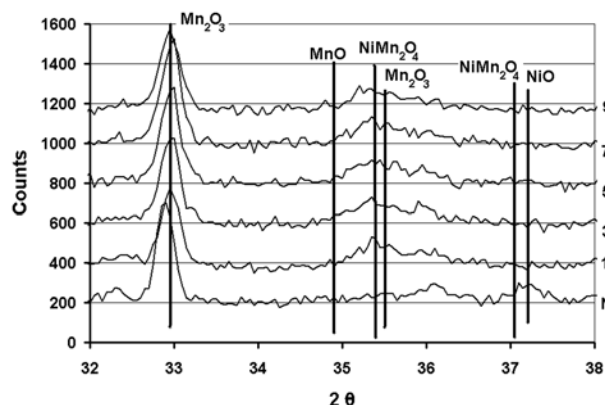


Fig. 8. X-ray powder diffraction patterns of mixtures of MnO and NiO milled into a zirconia vial for different times and heat treated at 500°C .

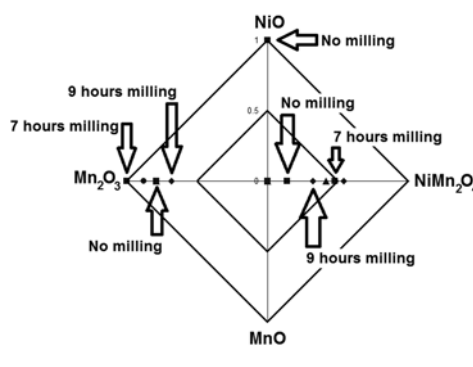


Fig. 9. Radar chart from the X-rays diffraction patterns shown in Fig. 8.

comparison with Fig. 6 that there is a dependence of the products on the milling time. Given that everything is a solid solution of NiO and manganese oxides and that NiMn_2O_4 is indeed $\text{NiO} + \text{Mn}_2\text{O}_3$, the presence of this late compound is important. The chart is made with peaks of relative intensity as explained above, and therefore the actual composition is not presented. However it is still clear that the results are affected by the MSP.

The milling process reduces the size of the particles increasing the specific area of the powders, which in turn promotes easier sintering. However this change corresponds only to geometrical aspects: particle surface area to bulk volume ratio. The milling process implies high pressures and high energy applied over small parts of the system at a given time, not just to reduce the particle size, but causing an incipient reaction. Fig. 10 shows ideal activities of different Mn-O compounds of a system of 2.55 mol of MnO and 0.45 mol of NiO in oxygen, calculated at 1 atmosphere and 10 atmospheres, squares are for Mn_2O_3 activity at 0.21 atmospheres. It can be noticed that Mn_2O_3 is free at around 500 °C at 1 atmosphere, when activity is unitary. Heat treatments conducted at 500 °C produced Mn_2O_3 even when arguments regarding Mn with a low diffusion coefficient suppose that this temperature is too low for activating the reaction that close of equilibrium. High pressures are also against Mn_2O_3 production because the temperature for achieving this compound is even higher. However the presence of Mn_2O_3 in this circumstance is a proof of energy stored in the system when milling was conducted, allowing the completion of the reaction during the heat treatment. There is also a noticeable tendency for the peak from MnO (at 34.93°) to disappear in favor of NiMn_2O_4 emerging (at 35.41°) looking as the MnO peak is shifting to the NiMn_2O_4 . This is only a tendency, but it is more noticeable on the samples that were heat treated at 700 °C. The activity of Mn_3O_4 also increases with temperature and pressure, which is important because this compound was also found in these samples.

Heat treatments conducted at 700 °C (Fig. 11) shown the presence of NiMn_2O_4 through the tendency described

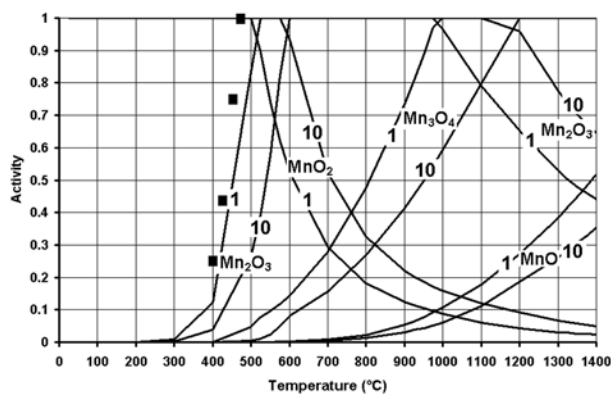


Fig. 10. Activities of different species calculated at 1 atmosphere (lines “1”) and 10 atmospheres (lines “10”), considering 2.55 mol of MnO and 0.45 mol of NiO in oxygen. Squares are for Mn_2O_3 at 0.21 atmospheres.

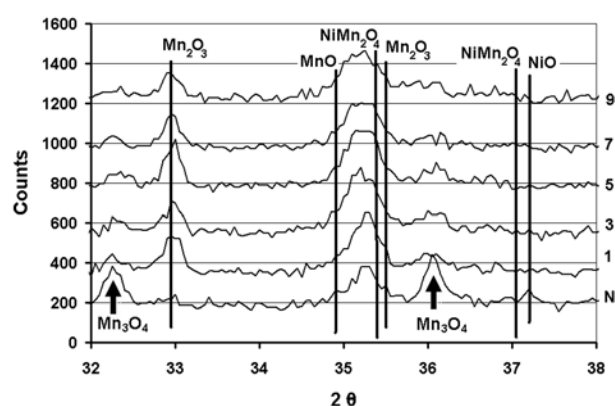


Fig. 11. X-ray powder diffraction patterns of mixtures of MnO and NiO milled into a zirconia vial for different times and heat treated at 700 °C.

above and a new peak of this compound at 18.28°. There still is Mn_2O_3 , which gives again a clue of the energy provided by the high energy milling process; higher temperatures provide conditions closer to equilibrium, and in this figure higher amount of Mn_2O_3 . 9 hours milling time produces more Mn_2O_3 than 1 hour. Mn_2O_3 does not necessary react to different oxides, but at a higher temperature it decreases because NiMn_2O_4 is indeed NiO and Mn_2O_3 . It is also very noticeable that Mn_3O_4 , could be ICSD 30005 or ICSD 31094, and it is produced at this temperature only with the non-milled powders. MnO is also a product after 9 hours (Fig. 11), but Mn_3O_4 is formed by MnO and Mn_2O_3 [21]. A radar diagram of the data shown in Fig. 11 is given on Fig. 12.

Mn_3O_4 is also present in the samples treated at 900 °C in the samples that were not milled (Fig. 13) as in the case of the 700 °C heat treatment. However, differences are less noticeable because the temperature was higher and conditions are closer to equilibrium. Something that can be noticed in the radar chart in Fig. 14 is that the relative magnitude of the peaks of NiMn_2O_4 in the non milling and 9 hours milling conditions are practically the same.

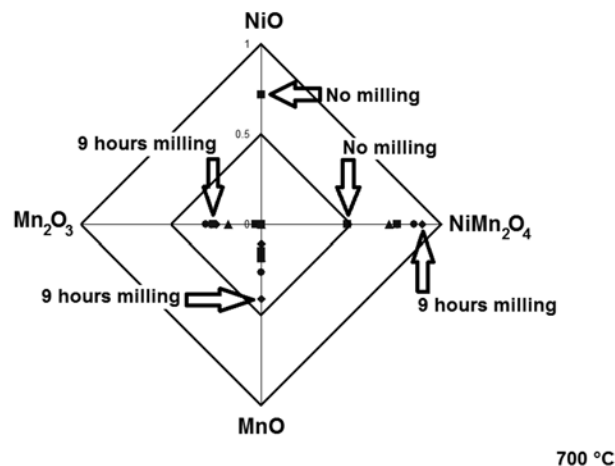


Fig. 12. Radar chart from the X-rays diffraction patterns shown in Fig. 11.

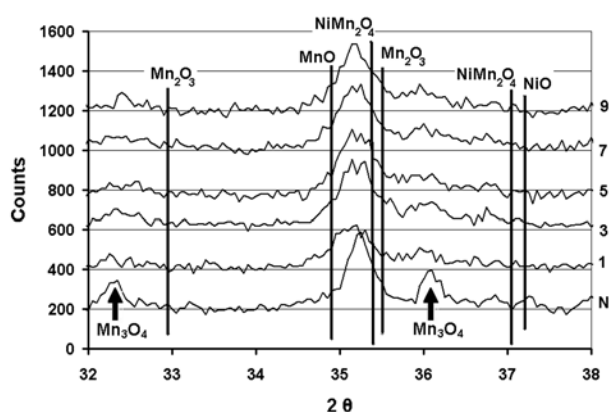


Fig. 13. X-ray powder diffraction patterns of mixtures of MnO and NiO milled into a zirconia vial for different times and heat treated at 900°C .

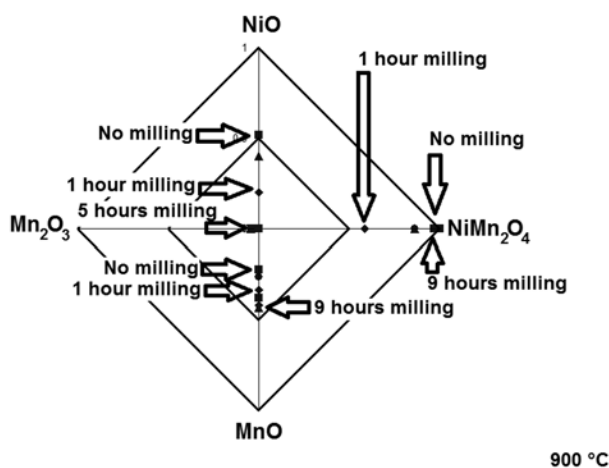


Fig. 14. Radar chart from the X-rays diffraction patterns shown in Fig. 13.

Mn_2O_3 is practically absent for all milling times and besides Mn_3O_4 there is NiO as well as MnO . The tests conducted at 900°C are close to an equilibrium line between a cubic spinel and a two-phase region of a mixture of spinel and NiO and that explains the variations in the peak intensities, even when a higher temperature supposes a reaction taking place closer to thermodynamic equilibrium. However it is clear that there is a difference among the MSP samples towards greater degree of reaction. The presence of Mn_3O_4 only in the non-milled cases is a proof by itself of the existence of changes due to the MSP. An apparent retrocession at 1 hour milling time is also explained by the reactions of the manganese oxides.

The effectiveness of MSP alone can be appreciated in Fig. 15, corresponding to a sample milled for one hour; some large particles of MnO are still present although most of them have been reduced to the size of NiO , about $10\ \mu\text{m}$. X-rays mappings of manganese, nickel and oxygen show that these elements are present in all the sample meaning that the compounds are well mixed and that Mn and Ni exist throughout the sample. Shaking produced

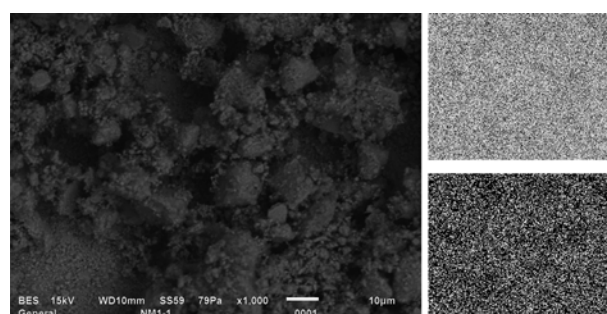


Fig. 15. SEM image of the powders after one hour of milling time; Mn and Ni X rays mappings are respectively shown above right and below.

a fine powder that is distributed throughout the sample while a reaction is taking place in all the particles, this is the reason for mapping without showing concentration profiles. Therefore SEM imaging and X ray mappings are illustrative of this condition, but only X rays diffraction can confirm the formation of the desired compounds.

Diffusion is a thermally-activated process following an Arrhenius expression. The temperature sensed in a system corresponds to the average of the temperature in all its elements, in the case of high-energy ball milling, the balls are hitting the powder and the temperature increases only at the impact sites, although the rest of the system might be unchanged. Reaction occurs only in those sites hit by hit. In a coarse example, it is possible to take an impact of an asteroid on a planet, the high energy hit is able to melt stone, indeed dating of these events is made after this melting, although the rest of the planet does not heat enough to melt and far from the impact site there is no temperature increase. This description is only an example, because the energy of an asteroid and relative masses of the bodies are not comparable to a ball - powders system where inertial forces are far lower. However, as in the planetary events, if the rock is melted it is because the necessary temperature was reached, and in the case of the powders, the only way to form Ni-Mn compounds is by providing the necessary energy, and being a diffusional process; only if the temperature was achieved.

Gulbransen and Meier [22] reported that Mn_2O_3 exists in the temperature range of $873\ \text{K}$ - $1073\ \text{K}$ (600°C - 800°C) and not above $1173\ \text{K}$ (900°C). MnO_2 converts to α - Mn_2O_3 above $723\ \text{K}$ (500°C). From $873\ \text{K}$ - $1213\ \text{K}$ (600°C - 1000°C) Mn_3O_4 reacts with MnO_2 to form Mn_2O_3 . Above $1213\ \text{K}$ MnO_3 (1000°C) breaks down to Mn_3O_4 and O_2 . These are the local temperatures that might be present during heating and that are of the same order as the temperatures chosen for the heat treatments where more spinel is formed. The samples that were just milled exhibited small amounts of spinel because many more hits are necessary and no more spinel is formed from hit sites where spinel is already present from a previous hit, which is the reason for a limit in the milling time. However, when heat treatments are conducted, more spinel is formed from the nuclei

left by the MSP.

Györgyfalva *et al.* [23] by means of thermal analysis and X-ray diffraction confirmed that single-phase, cubic-spinel-structured NiMn_2O_4 (2 : 1 Mn_2O_3 : NiO), begins to decompose into a rock salt and a second spinel-structured phase above 907 °C. This temperature is quite close to the proposed 900 °C, leading to the assumption that spinel will not be formed or any present spinel will be decomposed as Györgyfalva *et al.* proposed [23]. However, at the composition of $\text{Mn}/(\text{Mn} + \text{Ni})$ equal to 0.667 (Fig. 3) this temperature (907 °C) is practically, from a thermodynamic view, within the zone of a mixture of a solution of NiO-spinel and spinel, indeed were this late compound would mostly be present. Being that close to equilibrium, a longer time would be required to have actual decomposition.

Conclusions

Results clearly show the possibility of obtaining Ni-Mn spinel just by adding high-energy milling before conducting the heat treatment procedure. The effectiveness of the high-energy milling procedure is first demonstrated when despite the difference in size of the MnO and NiO powders, a uniform distribution of the type that is thermally achieved is obtained without external heating, from only the energy provided during the MSP. The results showed the formation of Mn_2O_3 after 3 hour of milling; other metastable phases could be present, but they were not detected. Given the wide region of the cubic spinel in the equilibrium diagram it is possible that other stoichiometries besides NiMn_2O_4 could be formed with peaks very close to this compound. A heat treatment at 500 °C for 3 hour shows the most advanced degree of reaction of the spinel. This condition can be taken as an example for designing MSP-heat treatment schedules where either processing time or temperature can be reduced when mechanical energy is added to the system previous to the heat treatment, although other characteristics such as controlling the grain growth via a temperature reduction could be more important than time.

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References

1. S. Fritsch, J. Sarrias, M. Brieu, J.J. Couderc, J.L. Baudour, E. Snoeck and A. Rousset, *Solid State Ionics* 109[3-4] (1998) 229-237.
2. E.D. Macklen in “Thermistors” (Electrochemical Publications Limited, 1979) p. 8-12.
3. E. Jabry, G. Boissier, A. Rousset, R. Carnet and A. Lagrange, *J. Phys. Colloques* 47[2] (1986); C1:843-847.
4. A.M. Bolarín-Miró, F. Sánchez-de-Jesús, S. Palomares, J. A. Aguilar and G. Torres-Villaseñor, *J. Alloys Compd.* 436 [1-2] (2007) 335-340.
5. C. Suryanarayana, *Prog. Mat. Sci.* 46[1-2] (2001) 1-184.
6. W. Tae Jeong, J. Hyun Joo and K. Sub Lee, *J. Alloys Compd.* 358[1-2] (2003) 294-301.
7. V. Šepelák, I. Bergmann, A. Feldhoff, P. Heitjans, F. Krumeich, D. Menzel, F.J. Litterst, S.J. Campbell and K.D. Becker, *J. Phys. Chem. C*, , 111[13] (2007) 5026-5033.
8. M. Alguero, J. Ricote, T. Hungria and A. Castro, *J. Chem. Mater.*, 19[20] (2007) 4982-4990.
9. H. Dutta, M. Sinha, Y.C. Lee and S.K. Pradhan, *Mat Chem Phys.* 105[1] (2007) 31-37.
10. A. Moure, T. Hungria, A. Castro, J. Galy, O. Peña, J. Tartaj and C. Moure, *Chem. Mater.* 22[9] (2010) 2908-2915.
11. D.G. Wickham, *J. Inorg. Nucl. Chem.* 26[8] (1964) 1369-1377.
12. G. Ashcroft, I. Terry and R. Gover, *J. Eur. Ceram. Soc.* 26[6] (2006) 901-908.
13. D. Stull and H. Prophet, *JANAF Thermochemical Tables*, Second edition, Standard Reference Data System (1971).
14. M. Chase, J. Curnutt, J. Downey, R. McDonald, A. Syverud and E. Valenzuela, *J. Phys. Chem. Ref. Data* 11[3] (1982) 695-940.
15. M.S.A. Karunaratne and R.C. Reed, *Acta Mater.* 51[10] (2003) 2905-2919.
16. P. Franke and R. Dieckmann, *Solid State Ionics* 26[2] (1988) 817-823.
17. N.L. Peterson, W.K. Chen and D. Wolf, *J. Phys. Chem. Solids* 41[7] (1980) 709-719.
18. W.K. Chen and N.L. Peterson, *J. Phys. Chem. Solids*, 36[10] (1975) 1097-1103.
19. N.L. Peterson and W.K. Chen, *J. Phys. Chem. Solids* 43[1] (1982) 29-38.
20. A.M. Bolarín, F. Sánchez, A. Ponce and E.E. Martínez, *Mat. Sci. Eng. A* 454-455 (2007) 69-74.
21. A.N. Grundy, B. Hallstedt and L. Gauckler, *J. Phase Equilib.* 24[1] (2003) 21-39.
22. E.A. Gulbransen and G.H. Meier in “Thermochemical stability diagrams for condensed phases and tabulation of volatile species over condensed phases for thirteen metal-oxygensilicon systems at 1000 and 1250 K” (Oak Ridge National Laboratories, 1989) p. 58.
23. G.D.C. Csete de Györgyfalva and I.M. Reaney, *J. Eur. Ceram. Soc.* 21[10-11] (2001) 2145-2148.