



## Mechanochemical Synthesis of Nanostructured $Mg_xNi_{1-x}O$ Compound by Mg-NiO Mixture

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### ABSTRACT

Synthesis of magnesium nickel oxide phase such as  $Mg_xNi_{1-x}O$  solid solutions has been studied in this research article using mechanochemical reaction between magnesium and nickel oxide. Mixtures of magnesium powder and nickel oxide (Mg+NiO) with stoichiometric compositions were milled for different times in a planetary ball mill. Reduction reaction of nickel oxide by magnesium via a mechanically induced self-sustaining reaction (MSR) was confirmed in the XRD measurements of the as-milled samples. Formation of nanostructured magnesium nickel oxide phases (such as  $Mg_{0.4}Ni_{0.6}O$  or  $MgNiO_2$ ) was observed after isothermal heating of the 30 minutes milled samples at 1000°C where nickel phase seems to disappear in XRD patterns. The traces of phases such as  $Mg_{0.4}Ni_{0.6}O$  or  $MgNiO_2$  were also observed in the as-milled mixtures. Therefore, the XRD results of the as-milled samples suggested that the formation of magnesium nickel oxide phases could be possible even after prolonged milling. The XRD and SEM results of both as-milled and isothermally heated samples indicated that the crystallite size and particle size of the final products reached to nanoscale after milling. Morphological and compositional evolution of the samples after heat treatment was monitored through SEM imaging and elemental analyses. The results confirmed that the composition of final product is close to  $Mg_{0.4}Ni_{0.6}O$  compound.

**Keywords:** Ball milling;  $Mg_xNi_{1-x}O$ ; Magnesium nickel oxide; Mechanically-induced self-sustaining reaction (MSR).

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### 1. Introduction

Nickel oxide (NiO) is a p-type transparent semiconductor with cation deficit and a wide band gap of 3.6-4 eV. Nickel oxide exhibits both rhombohedral and cubic structures, but the most prominent structure is cubic (rock salt crystalline structure) [1,2]. The crystalline structure of nickel oxide and magnesium oxide (MgO) are similar and their lattice parameters are very close so that NiO and MgO tend to form an ideal solid solution and a continuous series of  $Mg_xNi_{1-x}O$  solid solutions, with

$0 < x < 1$ , can be prepared [3-6]. Substitution of nickel ions by magnesium can stabilize the cubic structure [4]. The NiO-MgO system forms a continuous series of solid solutions with rock-salt crystal structure due to a small difference, of about 3 pm, in the ionic radii of  $Ni^{2+}$ ,  $Mg^{2+}$  ions 0.083 and 0.086 nm, respectively [4]. The MgO-NiO solid solutions belong to the class of the diluted face centered cubic (fcc) antiferromagnets. The  $Mg_{1-x}Ni_xO$  ( $0 < x < 1$ ) system is ideal for studying the effects of dilution on the magnetic properties and provides a

nice example of a diluted antiferromagnet [4-5,7]. Magnetic properties of the system vary strongly with the composition from antiferromagnetic like behavior, for pure NiO, to diamagnetic ionic insulator for pure MgO [7]. It has also been reported that nickel-magnesia solid solution has a high catalytic activity in CO<sub>2</sub> reforming of methane [3].

Synthesis of Mg<sub>x</sub>Ni<sub>1-x</sub>O solid solutions and NiO/MgO nanocomposites using ceramic technology, spray pyrolysis chemical process, exothermic reaction between an oxidizer (metal nitrates) and fuel (urea for example), and citrate precursor technique are already reported in literature [2,4,5-7]. The big challenge for production of synthesized compounds is using a simple and low cost procedure and decreasing the temperature (or time) of the post heat treatment.

Mechanochemical routes are suitable processing techniques for fabricating and syntheses of advanced materials, composites, nanoparticles and nanostructural materials [8-15]. The mechanical milling and high-energy ball milling procedures can be used to induce chemical reactions during milling at much lower temperatures than normally required by other techniques. Mechanochemical synthesis of materials is the general name given to the process of milling of powders involving chemical reactions occurring during milling. These reactions can be potentially used to reduce metal oxides and chlorides to pure metals, alloys, and compounds [8].

Depending on the milling conditions two entirely different reaction paths (modes) can be possible. The reaction may progress to a very small volume during each collision of milling balls, therefore resulting in a gradual transformation (reaction), or if the reaction enthalpy is sufficiently high (highly exothermic reaction), a self-propagating combustion reaction can initiate [8]. Therefore, if the reaction is highly exothermic, the impact of the milling balls can trigger a mechanically induced self-sustaining reaction (MSR) [8,16-17]. Depending on the previous results, such reactions are usually observed only in highly exothermic situations [8,16-20]. It has been proposed that a reaction becomes self-propagating if  $(-\Delta H_{298}^0)/(\sum C_{P_{298K}}) > 2000K$ , where  $-\Delta H_{298}^0$  is the enthalpy of reaction and  $\sum C_{P_{298K}}$  is total heat capacity of the products at 298 K [16-17].

The previous works on Zn-NiO system revealed some details on reaction progress and gradual

reduction of nickel oxide with pure zinc under both vacuum and open-valve conditions during high energy ball milling [21-22]. To the best of our knowledge, the effect of ball milling on the reduction reaction of nickel oxide by magnesium powder is not reported so far. It is, however, interesting to study the mechanochemical reaction of Mg-NiO with high-energy ball milling in order to elucidate the reaction mechanism (self-propagation combustion reaction or gradual reaction) and its products. Therefore, a systematic study on the mechanochemical reaction of Mg-NiO system using high energy ball milling to evaluate the possibility of formation of nanostructured magnesium nickel oxide phase (i.e. Mg<sub>x</sub>Ni<sub>1-x</sub>O) using mechanochemical synthesis is the concern of this work. In the present approach, the solid-state reduction of NiO by Mg with stoichiometric composition using a planetary ball mill (mechanochemical reaction) is investigated and the phase changes induced milling and after isothermal heating of as-milled samples are also studied.

## 2. Materials and Methods

Mixtures of nickel oxide (Merck, 100782) and magnesium powder (Merck, 8.18506) with stoichiometric composition were prepared based on the reaction (1).



Mixtures of raw materials were milled in the vacuumed cup using planetary ball mill (Farapazhouhesh, FP2 model) for different times (15, 30, 45, 60 and 120 minutes). The milling conditions for all runs were chosen based on the preliminary experimental runs. Those conditions were: the rotation speed of 600 rpm, high-chromium steel balls (20 mm diameter), high-chromium steel milling chamber and ball-to-powder weight ratio of 40:1. After finishing each milling run, the cups were opened in air atmosphere and as-milled powders gathered. Then the milling cups and balls was washed with ethanol and dried.

Isothermal runs were performed in a tubular furnace (Lenton, LFT, 16180) with samples being held at different temperatures (400 °C and 1000 °C) for an hour and then allowed to cool to room temperature all under the flow of pure argon. Products were analysed using Xray diffraction (XRD, Philips Analytical, CoK $\alpha$  radiation, 40 kV, 40 mA, X'Pert APD) over 2 $\theta$  range of 40100° using

a step size of  $0.05^\circ$ . Microstructural analysis of the samples was performed using field emission scanning electron microscope (FESEM, TESCAN MIRA3 LMU).

The crystallite size of the final products in the as-milled samples was calculated using the well-known Scherrer equation. In addition, the microstrain of the as-milled Mg-NiO samples can be calculated from the following equation [1]:

$$\varepsilon = \frac{\beta_{\frac{1}{2}}}{4 \tan \theta} \quad (\text{Eq. 2})$$

Where,  $\beta_{0.5}$  in the equation (1), is the full-width at half-maximum of (111) and (200) planes for MgO peaks and (111) for nickel peak in as-milled samples and  $\theta$  is the Bragg angle. Finally, the dislocation density of the as-milled samples was determined by the Williamson and Smallman's relation (equation 2) [1]. In the equation (2),  $\delta$  represents the defect density in the crystals of the as-milled samples and  $D$  is the crystallite size.

$$\delta = \frac{1}{D^2} \quad (\text{Eq. 3})$$

### 3. Results and Discussion

Thermodynamic calculations for stoichiometric Mg-NiO mixture show that  $\Delta H_{298K}^0$  for reaction (1) is negative at room temperature ( $\Delta H_{298K}^0 = -361\text{kJ}$ ), also the amount of  $(-\Delta H_{298K}^0)/(\sum C_{P_{298K}})$

ratio is about 5400K [23]. Therefore, the reaction (1) is highly exothermic and the initiation of mechanically induced self-sustaining reaction (MSR) is anticipated during ball milling of a stoichiometric mixture of nickel oxide and magnesium powder.

Fig.1 shows the XRD patterns of Mg-NiO powder mixtures with stoichiometric composition as a function of milling time (the as-milled samples). Presence of new peaks corresponding to nickel phase (JCPDS No. 004-0850) and MgO phase (JCPDS No.075-1525) indicates that the reduction reaction occurs after 15 minutes milling. Therefore, these patterns justify the thermodynamic calculations and show that the reduction reaction of nickel oxide by magnesium powder can take place through high energy ball milling of the Mg-NiO mixture. A previous study on stoichiometric mixture of  $\text{SrSO}_4$  and Mg reveals a mechanically induced self-sustaining reaction (MSR) after milling for less than 10 min in a planetary mill [19]. However, the MSR reaction was not observed in the Zn-NiO mixtures neither on vacuumed nor open-valve milling conditions once those stoichiometric mixtures were milled using planetary ball mill [21-22].

XRD Results of Fig.1 show that the nickel peak at about  $2\theta=52^\circ$  shifts slightly to lower degrees and its relative intensity decreases with increasing milling

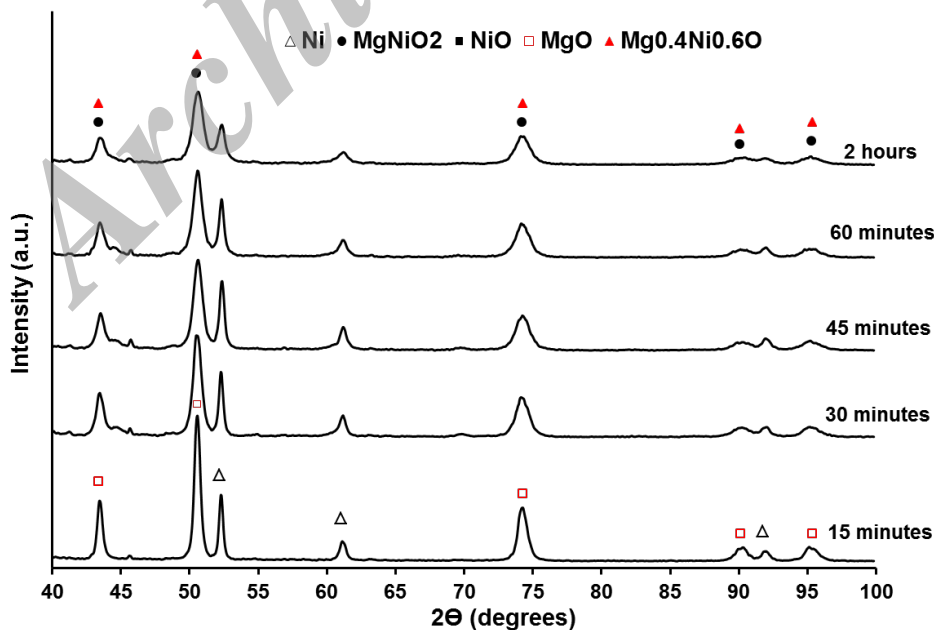


Fig. 1- XRD patterns of the Mg-NiO system as a function of milling time (the as-milled samples).

time. Same scenarios are observed at about  $2\theta=50^\circ$  and  $2\theta=74^\circ$  with increasing milling time. Decrease in relative intensity and peak broadening for nickel and magnesium oxide (MgO) with increasing milling time is clearly observed in Fig.1. These may be related to the reduction of mean crystallite size. On the other hand, signs of new phases (i.e. magnesium nickel oxide phases) also appear when milling is prolonged, suggesting that reaction(s) may occur during milling Mg-NiO mixture.

Table (1) lists the mean crystallite sizes of the nickel and magnesium oxide (the products of reaction 1) for different milling times. The crystallite size of nickel phase (product of reaction 1) was calculated using Scherrer equation based on its main peak (i.e.  $2\theta=52.178^\circ$ ). The same calculations were done for (111) and (200) peaks of magnesium oxide (i.e.  $2\theta=43.4$  and  $2\theta=50.55$ ). The results of Table (1) show that with increasing milling time, the crystallite sizes of both magnesium oxide and nickel phase is decreased to nanoscale, confirming the potentiality of the employed mechanical activation

Table 1. The values of crystallite size of nickel and MgO phases based on XRD patterns in figure 1.

Milling time	Crystallite size (nm)		
	Magnesium oxide		Nickel phase
	(111) plane	(200) plane	(111) plane
15 minutes	69.32	64.27	137.95
30 minutes	44.69	39.3	107.38
45 minutes	41.97	32.49	84.33
60 minutes	42.17	33.5	72.61
2 hours	29.9	28.76	42.6

for synthesis of nanostructured materials. The data of Table (1) shows that the crystallite size of nickel phase is larger than magnesium oxide.

Microstrains and dislocation densities for all as-milled mixtures (computed for the major magnesium oxide and nickel peaks) are listed in Table (2). The dislocation densities are calculated using data in Table (1). Table (2) shows that microstrain and dislocation density increase dramatically with increasing milling time. These data confirm the effects of mechanical activation and impacts of balls on the powders during high energy ball milling. The results of Table (2) show that nickel phase is much more strained than the magnesium phase. After 2 hours of milling, dislocation density for nickel phase is about ten times larger than 15 minutes milled sample. On the other hand, however, the dislocation density of magnesium oxide shows about fivefold increase for the same period of milling time. Therefore, higher levels of work hardening are expected in nickel phase as compared to magnesium oxide. Nickel is a faced-centred-cubic metal and can withstand more hardening than magnesium oxide which is non-metallic with NaCl type structure.

Fig.2 shows the SEM micrographs of the as-milled samples. Decreasing particle size with milling progress is clearly observed in the micrographs of as-milled samples. It should be noted that after milling, the phases are intimately mixed on a sub-micron scale and are hardly distinguishable by SEM without proper sample preparation (mounting and backthinning).

The EDS analyses of the as-milled samples (not shown here) reveal that the milled structure is mainly comprised of Ni, O, and Mg. Recalling XRD finding (Fig.1), these fine particles in SEM

Table 2- The values of microstrain and dislocation density of nickel and MgO phase based on XRD patters in figure 1

Milling time	Microstrain ( $10^{-3}$ )			Dislocation density ( $10^{14}$ Lines/m <sup>2</sup> )		
	Magnesium oxide		Nickel phase	Magnesium oxide		Nickel phase
	(111) plane	(200) plane	(111) plane	(111) plane	(200) plane	(111) plane
15 minutes	1.57	2.94	0.6654	2.081	2.421	0.5255
30 minutes	2.433	2.4	0.8492	5	6.475	0.86726
45 minutes	2.588	2.671	1.0826	5.677	9.473	1.406
60 minutes	2.582	2.829	1.2595	5.623	8.91	1.8967
2 hours	3.6327	3.28	2.147	11.18	12.09	5.51

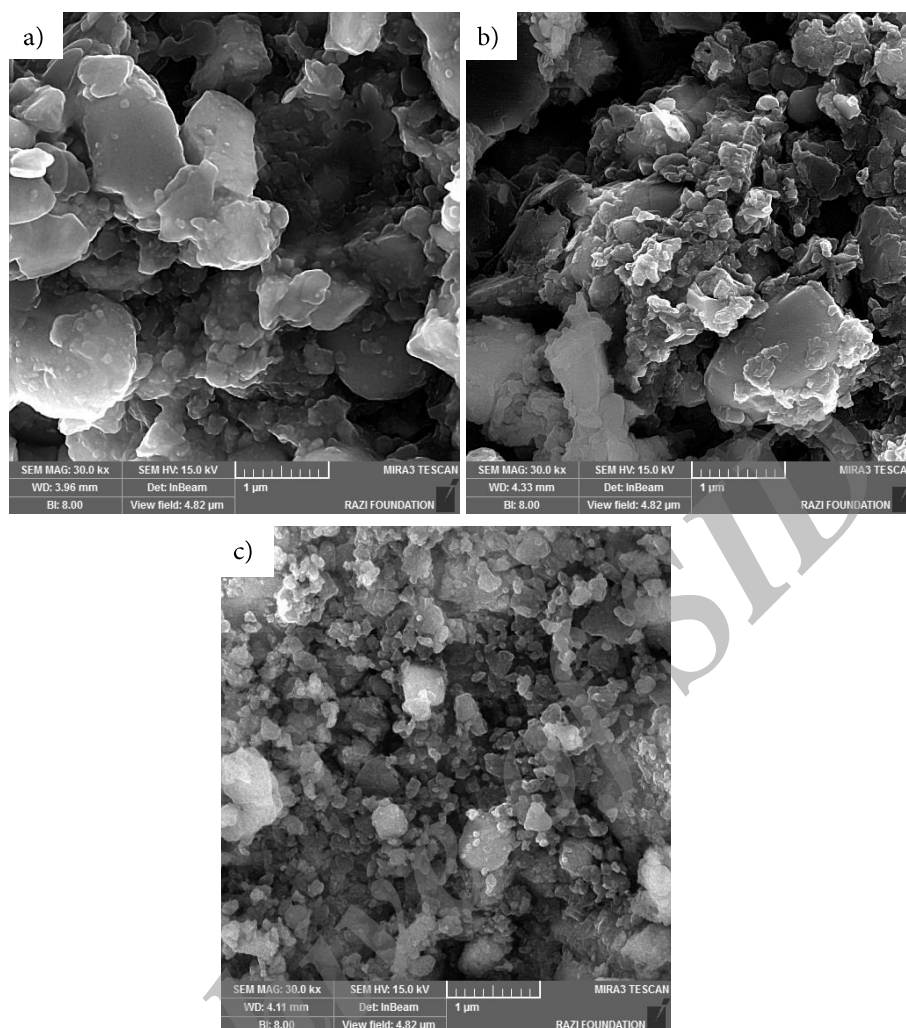


Fig. 2- SEM micrographs of the Mg-NiO for different milling time (the as-milled samples). (a) 15 minutes milling, (b) 30 minutes milling and (c) 60 minutes milling.

micrographs should be mixtures of magnesium oxide and nickel phases. Based on table (1), nickel crystallites are larger than magnesium oxide crystallites. Thus, in SEM photographs (Fig.2), larger particles must be nickel phase produced during ball milling. It is worthy to know that from crystallography point of view, nickel has faced-centred-cubic structure and is more ductile than magnesium oxide (NaCl structure). Therefore, nickel particles are expected to show more tolerance while being impinged by balls thus resisting against excessive size reductions. SEM micrographs of Fig.2 justify the XRD findings, through indicating the significant role of ball milling on the refining the crystallite size and nanostructure formation.

To study the stability of the products and in order to investigate the possibility of formation of

other phases in the system, samples milled for 30 min were isothermally heated at 400°C and 1000°C for 1 hour in argon atmosphere. Then, the system was cooled off keeping the argon flow. Products were analysed by XRD with results depicted in Fig. 3.

The peaks of magnesium oxide and nickel phases (products of reaction 1) are detected in both samples isothermally heated under argon atmosphere (Fig.3). As compared to 400 °C isothermally heated sample, the relative intensity of nickel phase decreased dramatically after when treated at 1000°C for one hour. The relative intensities of the main peaks at about  $2\theta=43^\circ$ ,  $50^\circ$ , and  $74^\circ$  are increased and they are slightly shifted to lower degrees after heating at 1000 °C. Also, the peaks become sharper and narrower as compared to 400°C heated sample.

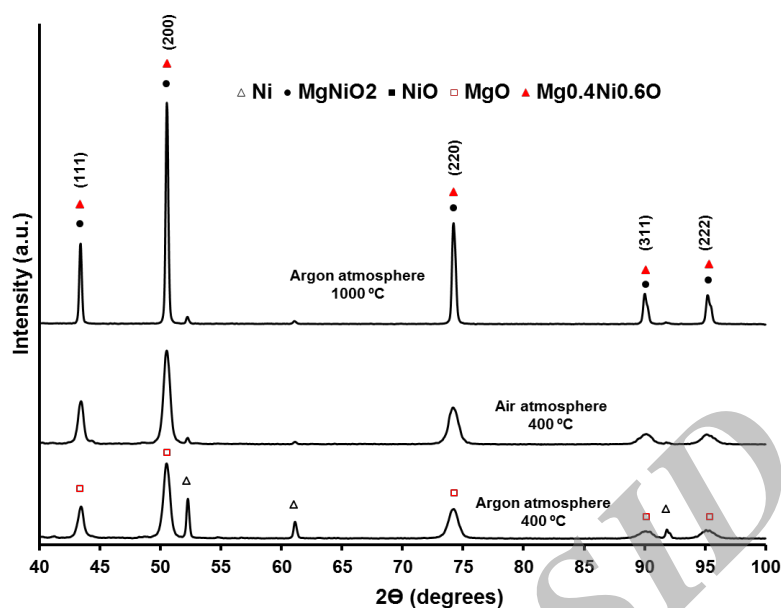


Fig. 3- XRD patterns of the 30 minutes as-milled samples after 1 hour heating in argon and air atmospheres at different temperatures.

Increasing the heating temperature leads to better crystallisation of the products. However, shift of the main peaks and reduced nickel peak intensity at 1000°C is the sign of occurrence of a reaction in the system in the isothermally heated samples under argon atmosphere. The same peak shifts were observed in as-milled samples (Fig.1) where the peak at about 50° shifted slightly to lower degrees with increasing of milling time. This indicates that milling triggers a reaction in the system even in milling times as short as 15 minutes. The previous report show a peak shift related to the formation of  $Mg_xNi_{1-x}O$  films ( $x=0.25-0.56$ ) during sintering of a mixture of high purity MgO and NiO powders where substitution of Ni atoms by Mg atoms results in changes of peak position [2].

For the sake of comparison, the 30 minutes as-milled sample was also prepared and heated isothermally at 400 °C for one hour in ambient air with patterns embedded in Fig.3. Here, the peaks corresponding to nickel phase are almost disappeared (very small peaks are detectable), revealing a pattern quite similar to that of 400 °C heated sample under flow of argon.

It is worthy to note that the main peak of nickel oxide (JCPDS No.47-1049) occurs at  $2\theta=50.705^\circ$  ( $d=2.089\text{\AA}$ , (200) planes), whilst the main magnesium oxide peak (JCPDS No.75-1525) is observed at  $2\theta=50.55^\circ$  ( $d=2.095\text{\AA}$ , for (200) planes). Nickel oxide (NiO) with cubic structure and magnesium oxide (MgO) have rock

salt crystalline structures with very close lattice parameters ( $4.1771\text{\AA}$  and  $4.19\text{\AA}$  for NiO and MgO respectively) and bond distances ( $2.1$  and  $2.11\text{\AA}$  for NiO and MgO respectively) [1,2,6]. For this reason and also due to the small difference in ionic radii of  $Ni^{2+}$  and  $Mg^{2+}$  ions (about  $0.02\text{\AA}$ ), they can readily substitute each other and form a solid solution [4-5,7].

Fig.1 shows that relative intensity of main nickel peak ( $2\theta=52.178^\circ$ ) has decreased after 30 minutes milling when compared to 15 minutes as-milled sample. The crystallite size is also decreased with increasing milling time as indicated in table (1). Isothermal heating in ambient air (Fig.3) can lead to oxidization of finer nickel particles in 30 minutes milled sample therefore improving the chance of formation of a solid solution between the produced nickel oxide and remained MgO. It is clear that fine nickel particles also can react with magnesium oxide during isothermal heating process under the flow of argon, thus improving the chance of nickel diffusion into magnesium oxide particles during treatment at 1000°C.

A major characteristic feature of all solid-state reactions is that they involve the formation of products phase(s) at the interface of reactants [8]. The repeated welding and fracturing processes of all involved powder particles during mechanical alloying (mechanical milling) processes leads to reduction in particle size of the powders, therefore it can increase the contact area between the

reactant powder particles. Therefore, it allows the fresh surfaces to come into contact repeatedly and this provides the reaction to progress without the necessity for diffusion through the solid product layer. In addition, the high defect densities (such as dislocations, vacancies and so on) induced by mechanical alloying (milling) can accelerate the diffusion process [8]. It seems that same scenarios can occur during ball milling of Mg-NiO system with stoichiometric composition. Therefore, the particles refinement and consequent reduction in diffusion distances (due to high defect densities and microstructural refinement) can provide the possibility of diffusion of nickel into magnesium oxide during heat treatment of 30 minutes milled mixture under flow of argon atmosphere (Fig.3).

The XRD data files show that the magnesium nickel oxide phases such as  $Mg_{0.4}Ni_{0.6}O$  (JCPDS No. 34-0410) or  $MgNiO_2$  (JCPDS No. 24-0712) satisfy the XRD results of Fig.3. The  $Mg_{0.4}Ni_{0.6}O$  phase is a member of  $Mg_xNi_{1-x}O$  system with cubic structure. Based on the previous results, the lattice parameter of the  $Mg_xNi_{1-x}O$  system depends linearly on the composition [4-5,7].  $MgNiO_2$  has a lattice constant of 4.1926Å with the main peak at  $2\theta=50.498^\circ$  ( $d=2.097\text{\AA}$ , (200) planes), whilst the value of  $Mg_{0.4}Ni_{0.6}O$  is 4.19Å and its main peak occurs at  $2\theta=50.55^\circ$  (for Co radiation,  $d=2.095\text{\AA}$ , (200) planes) [24,25]. These values are very close to magnesium oxide parameters (JCPDS No. 75-1525). Therefore, if nickel phase can diffuse into magnesium oxide during heating at 1000°C under flow of argon atmosphere, magnesium nickel oxide compounds may be formed. Heating 30 minutes milled samples in ambient air, results in formation of NiO due to oxidation of the finer nickel particles and formation of solid solution with remained magnesium oxide. The previous results showed that the formation of nickel zinc oxide ( $Ni_{0.6}Zn_{0.4}O$ ) during isothermal heating of un-milled samples and as-milled Zn-NiO mixtures [21-22] is due to substitution of Ni (ionic radius: 0.69Å) with Zn (ionic radius: 0.74 Å) [26-27].

Under flow of argon, nickel phase observed fairly in the isothermally heated sample at 1000°C in Mg-NiO system. Formation of  $Mg_{0.4}Ni_{0.6}O$  or  $MgNiO_2$  seems to occur after heating the 30 minutes as-milled mixture at temperature of 400 °C and the peaks well crystallized at temperature of 1000 °C. Fig.1 indicates the possibility of the presence of magnesium nickel oxide ( $Mg_{0.4}Ni_{0.6}O$  or  $MgNiO_2$ ) in the as-milled mixtures, those phases may occur

just after 30 minutes milling time.

The lattice parameter of the 30 minutes milled mixture after 1 hour heating at 1000 °C under flow of argon was computed to be 4.188 Å, close to that of  $Mg_{0.4}Ni_{0.6}O$ . The color of 30 minutes milled sample after isothermal heating at 1000 °C was greenish. It should be noted that the color of the standard sample is green [25] and it is declared that these  $Ni_xMg_{1-x}O$  solid solutions have greenish color and their color intensities depend on the nickel content [5]. Therefore, it seems that the final product after isothermal heating at 1000 °C is  $Mg_{0.4}Ni_{0.6}O$ .

Morphologies of the 30-minutes milled samples after one-hour heating under different condition are shown in figure 4a-c. The heating atmosphere (argon or ambient) at 400 °C, show to impose no effect on the morphology of the products, while heating at 1000 °C affects particle morphology and size (Fig. 4.c). The elemental map (Fig. 4.d) of the sample after being heated at 1000 °C (argon flow) reveals uniform distribution of magnesium and nickel along with oxygen throughout the entire sample. The corresponding EDS spectrum (Fig.4.e) reveals the peaks of magnesium, nickel and oxygen phases in agreement with XRD findings. These results can confirm formation magnesium nickel oxide phase in the samples.

Previous reports on Zn-NiO system confirm the gradual progress of the reaction during high energy ball milling with mixtures of ZnO and  $Ni_{0.6}Zn_{0.4}O$  phases as the main products [21-22]. The reaction of nickel oxide with magnesium (reaction 1) is highly exothermic compared to the reduction reaction in Zn-NiO system, therefore the XRD patterns (Fig.1) showed that reduction reaction in Mg-NiO system could be completed within 15 minutes.

#### 4. Conclusions

The results revealed the reduction reaction between nickel oxide and magnesium could be completed within 15 minutes of milling and initiation of MSR occurred during high energy ball milling of the stoichiometric composition of Mg-NiO. It seems that the formation of magnesium nickel oxide phases (such as  $Mg_{0.4}Ni_{0.6}O$  or  $MgNiO_2$ ) to occur after heating the 30 minutes as-milled mixture at temperature of 400 °C. The traces of nickel phase were almost disappeared after isothermal heating the 30 minutes milled sample at temperature of 1000 °C under flow of argon atmosphere. Although the traces of nickel phase

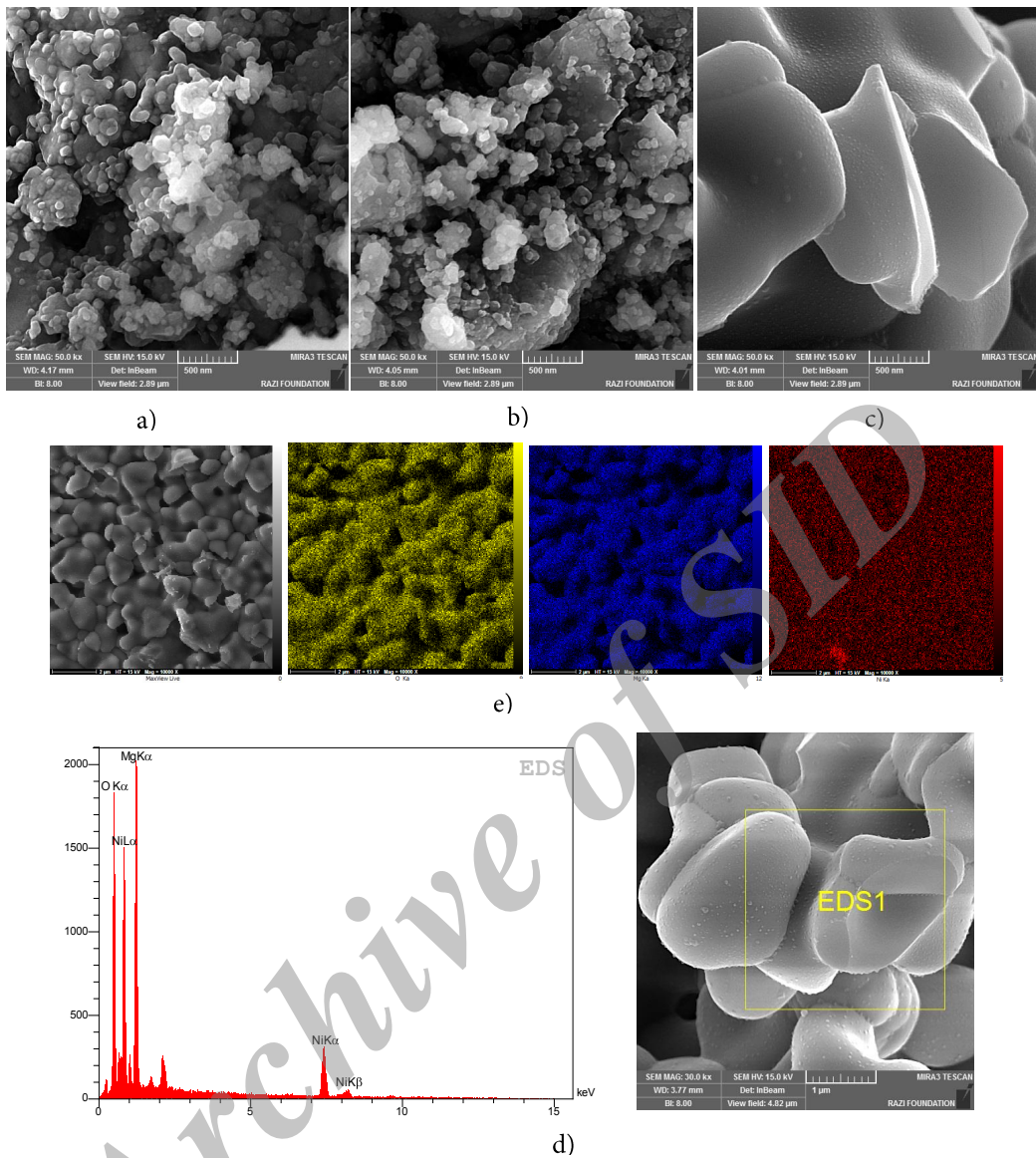


Fig. 4- SEM micrographs of the 30 minutes milled mixture after one hour heating at different conditions. (a) 400 °C in argon atmosphere, (b) 400 °C in ambient air, (c) 1000 °C in argon atmosphere, (d) elemental map analysis of the heated sample at 1000 °C in argon atmosphere, (e) EDS analysis of the heated sample at 1000 °C in argon atmosphere.

and magnesium oxide are observed after 15 minutes of milling however it seems that the formation of magnesium nickel oxide phases (such as  $Mg_{0.4}Ni_{0.6}O$  or  $MgNiO_2$ ) to be possible after prolonging milling time. Increasing the milling time led to refine the crystallite size of product phases and the amount of microstrains and dislocation density in the nickel phase were much more than magnesium phase. The computed lattice parameter of the 30 minutes milled sample after isothermal heating at 1000 °C was very close to the value of  $Mg_{0.4}Ni_{0.6}O$ .

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