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Preparation of nanostructured nickel aluminate spinel powder from spent NiO/Al$_2$O$_3$ catalyst by mechano-chemical synthesis

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ABSTRACT

In this paper, the possibility of mechano-chemical synthesis, as a single step process for preparation of nanostructured nickel aluminate spinel powder from NiO/Al$_2$O$_3$ spent catalyst was investigated. Powder samples were characterized in terms of composition, morphology, structure, particle size and surface area using complementary techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), differential thermal analysis (DTA) and volumetric adsorption of nitrogen. It was found that formation of spinel was possible after 60 h of milling with no heat treatment. Additionally, influence of mechanical activation on the heat treatment temperature was discussed. It was observed that heat treatment of 15 h milled sample at 1100 °C is enough to produce nickel aluminate spinel. A product of direct mechanical milling showed higher value of surface area (42.3 m^2/g) and smaller crystallite size (12 nm) as compared to the heat treated product.

1. Introduction

Alumina-supported nickel catalyst is an important catalyst in various petrochemical industrial processes [1]. After a certain period, depending on the operating conditions, destructive effects such as coking, poisoning, sintering and contamination would decrease its catalytic activity [2]. Deactivated catalysts undergo regeneration for several times; however, the number of regeneration cycles is limited since the process effectively removes the coke and not the deposited heavy metals. Therefore, after several regeneration cycles, accumulation of heavy metals deactivate the catalyst to a level that its regeneration is not financially favorable and it should be discharged and replaced by fresh catalyst [3,4]. Release of hazardous heavy metal content of the spent catalysts to the environment has raised serious concerns during the last decades leading to strict legislations on handling and disposal of this kind of wastes [5]. Recently, extensive studies have been conducted to establish possible environmental friendly treatments for recycling of the spent catalysts [6].

On the other hand, NiO/Al$_2$O$_3$ catalyst has the precursor constituents to produce nickel aluminate (NiAl$_2$O$_4$) spinel. NiAl$_2$O$_4$ is a partially reverse spinel with nickel ions in octahedral sites and aluminum ions in tetrahedral sites [7]. Due to its high melting point, high activity and resistance to corrosion, nickel aluminate has been used in various catalytic applications and high temperature fuel cells. It is also proposed as a promising anode for aluminum production [8,9]. The inverse spinel structure shows ferromagnetic behavior and if it is synthesized as nanocrystalline, nickel aluminate will demonstrate unique potential application in high-density magnetic recording, microwave devices and magnetic fluids [10]. NiAl$_2$O$_4$ can be prepared by different methods such as solid state reaction [11], impregnation [12], co-precipitation [13], sol–gel [14] and microwave [15]. Formation of NiAl$_2$O$_4$ by solid state reaction according to Eq. (1) involves sintering of mixture of metal oxides at high temperature [11]. However, this method requires high sintering temperatures and long reaction times, resulting in low NiAl$_2$O$_4$ surface area, i.e., the nanostructured product could not be formed. Mechanical alloying and mechano-chemical synthesis are novel solid state processing routes for producing nanostructured materials. It has been shown that during milling enhanced reaction rates can be achieved and dynamically maintained as a result of microstructural refinement and mixing processes accompanying repeated fracture, welding, and deformation of particles during collision events [16]. Also, reactivity of the milled powders can be enhanced by mechanical activation and hence, the temperature in subsequent heat treatment steps will be reduced [17]. In a previous work by Han et al. [18], effect of excess NiO on the synthesis of NiAl$_2$O$_4$ through solid state reaction was investigated. They found that the milling time and starting materials had an important effect on the excess of NiO.

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$$NiO + Al_2O_3 = NiAl_2O_4 \tag{1}$$

Since the capability of mechano-chemical synthesis for single step processing of nanostructured nickel aluminate spinel has not been investigated, present study focuses on the mechanical milling of spent NiO/Al_2O_3 catalyst and production of nanostructured nickel aluminate spinel. Furthermore, direct formation of spinel through mechano-chemical synthesis was compared with the mechanical activation and the consequent heat treatment procedure; with particular attention to the activation process by thermal analysis technique.

2. Experimental procedure

Starting materials were spent catalyst with the composition shown in Table 1 and NiO powder with 99.8 pct purity (finer than 50 μm, Charloa Co.). It should be mentioned that as a pretreatment the catalyst was firstly roasted in a muffle furnace at 500 °C for 5 h to remove coke, sulfur and oil. Then, it was crushed and sieved. The powder particle size utilized for all subsequent steps was 37–74 μm ($-200 + 400$ mesh). Since, the NiO content of the catalyst sample was not enough for the formation of spinel structure, excess NiO was added to the sample to satisfy the stoichiometric condition (Ni/Al molar ratio of 1:2). The mixture of catalyst and NiO powder was milled for ca. 60 h in a high-energy planetary ball mill under air atmosphere. The ball-to-powder weight ratio and rotation speed were 30:1 and 300 rpm, respectively.

The non-isothermal reaction of the powder mixtures was investigated by DTA (Netzsch STA 409 PC/PG instrument) in air atmosphere at temperature up to 1400 °C with heating rate of $10 \, °C\,min^{-1}$. Additionally, isothermal heat treatment was done under air atmosphere in a furnace with a heating rate of $10 \, °C\,min^{-1}$ at various temperatures for 2 h.

The phase identification of the crystalline products was carried out by XRD (Philips PW-3710) using Cu K_{α} radiation ($\lambda = 0.17407$ nm). The instrumental-broadening corrected line profile breadth of each reflection was calculated by applying Warren's method [19]. The average crystallite size and lattice micro-strains were obtained using Williamson–Hall plot [20]. The microstructure of the samples were examined by SEM (Hitachi, S-4800) equipped with an energy dispersive spectrometer (EDS) (Bruker AXS, XFlash Detector 4010) and TEM (Philips CM200, operated at 200 kV). The average specific surface area of the powders was determined by nitrogen adsorption at 77 K (Micromeritics Tristar II 3020) employing the BET isotherm equation.

3. Results and discussion

3.1. Mechano-chemical synthesis

Fig. 1 shows XRD patterns of the samples milled at various times, revealing the structural evolution as milling progressed in the powder mixture. With increasing the milling time, the peaks of Al_2O_3 and NiO were gradually broadened and their intensities decreased. The broadening of the peaks is mainly due to the microstructure refinement and internal lattice strain, which is attributed to high energy ball milling. The $NiAl_2O_4$ peaks appeared at ca. 15 to 20 h of milling time. Further increase in milling time resulted in an increase in the $NiAl_2O_4$ peaks intensities, and the single phase $NiAl_2O_4$ was obtained after 60 h milling, when the powder mixture was completely converted into nickel aluminate spinel. The average crystallite size and lattice strain of the final product was calculated to be 12 nm and 1.1%, respectively, using Williamson–Hall method.

It was reported by Pettit et al. [11] that the formation of $NiAl_2O_4$ spinel from Al_2O_3 and NiO requires high temperatures of ca. 1200

Table 1
Chemical analysis of the spent catalyst.

Element*	Al	Ni	Fe	Cr	Ca	Mo	Co	V
Weight%	43.31	12.20	0.05	0.10	0.48	0.06	0.05	0.02

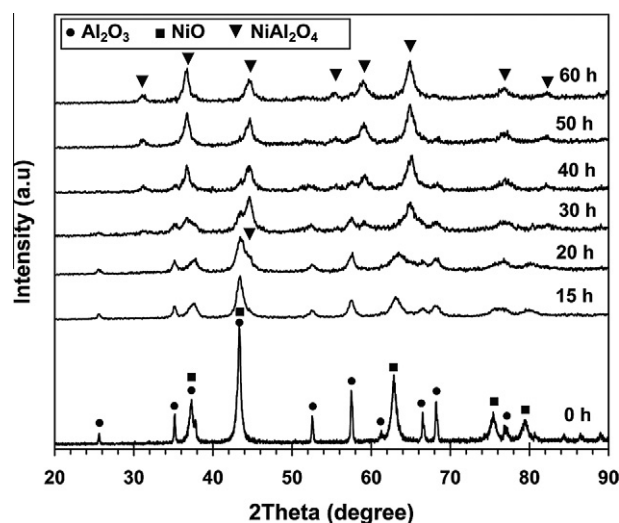* Oxygen contents are not included.

Fig. 1. XRD patterns of milled powder mixture after different milling times.

to 1500 °C for a long period of time. However, in the present study, the reaction occurred in a very low temperature (near the room temperature) by mechanical milling. There are explanations for this observation. It was suggested by Pettit et al. [11] that diffusion of aluminum ions through the spinel layer is the rate controlling step in the $NiAl_2O_4$ formation. It should be noted that mechanical milling supplied enough Al ions around the NiO particles. Indeed, mechanical milling decreased the particle size to the submicron scale and NiO particles were highly dispersed between the Al_2O_3 particles. Furthermore, transport of aluminum ions depends on the available diffusion path and their diffusivity along the path. Regarding to the decrease in crystallite size and the increase in internal lattice strain, mechanical milling enhanced the diffusivity by creating short diffusion paths, such as point defects, grain boundaries and dislocations [16]. Additionally, the extent of the reaction at the center of spinel is limited, due to the long path for the aluminum ions transferring through the product. However, mechanical milling allows the reaction to proceed by increasing the number of fractures in the product layers as well as creating fast diffusion paths. As a result, the reaction between NiO and Al_2O_3 occurs even at low temperatures.

Figs. 2–4 show the SEM images of powder mixture at different stages of milling. Fig. 2 shows the particle morphology of the powder at the early stages of milling, i.e., after 1 h of milling. The initial powders had different size distributions and shapes. There were some individual fine particles and the rest were agglomerated. Based on the image at a higher magnification and corresponding X-ray mapping images of Al, O and Ni elements, the elements were not homogeneously distributed on an atomic scale at the initial milling stage. With further milling up to 10 h, the mean particle size decreased. The particles also became more uniform and spherical (Fig. 3(a)). Fig. 3(b) shows the morphology of the particles during milling, i.e., 30 h of milling. In comparison with the microstructure of the powder mixture before the reaction in Fig. 3(a), some new bright phases with different morphology could be
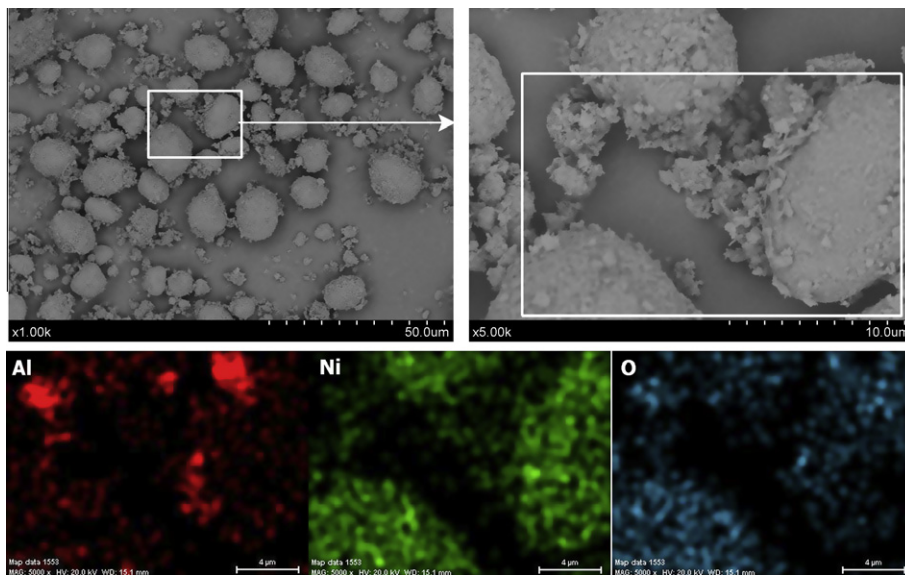
Fig. 2. SEM image of 1 h milled powder mixture and the corresponding Al, O and Ni mapping images from rectangle area.
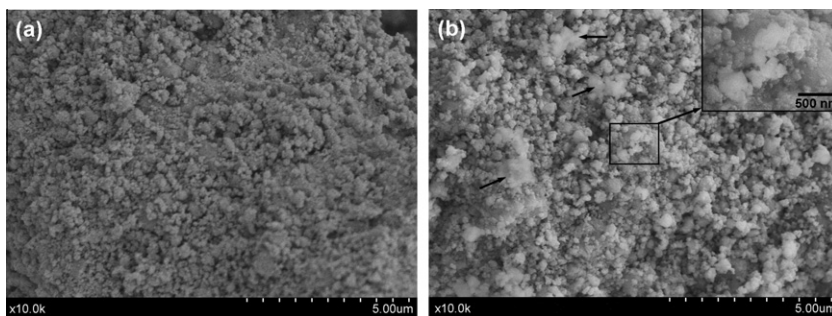
Fig. 3. SEM images of milled powder mixtures of NiO and spent catalyst after milling for (a) 10 and (b) 30 h.
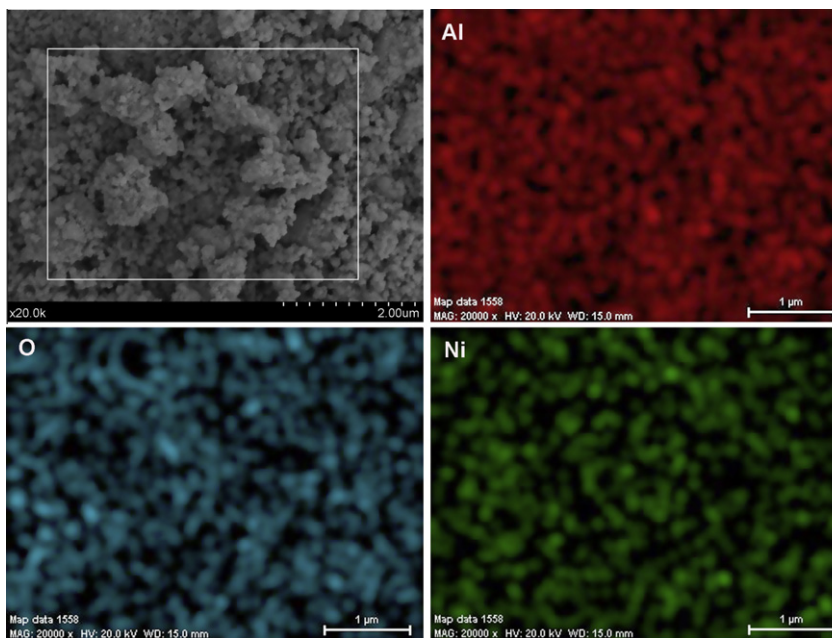
Fig. 4. SEM image of 60 h milled powder mixture and the corresponding Al, O and Ni mapping images from rectangle area.
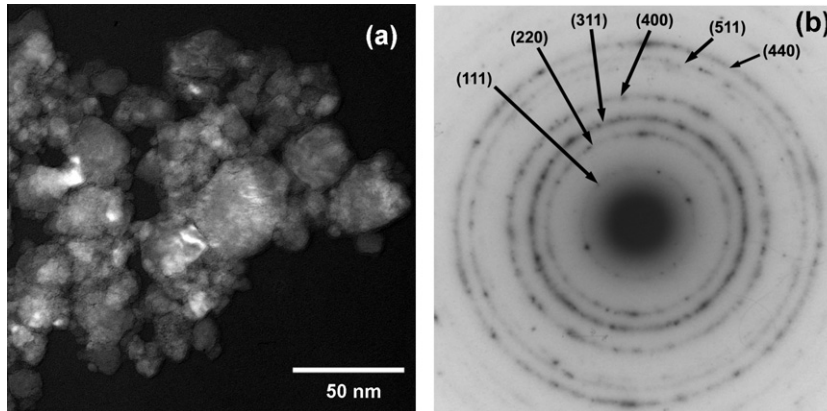
Fig. 5. TEM image of NiAl$_2$O$_4$ after 60 h milling (a) bright field image and (b) SAD pattern.

observed in the micrograph which is indicated by arrows. The high magnification image shown in the inset of Fig. 3(b) clearly exhibits one of these ultra fine particles. According to the XRD pattern of the mixture in Fig. 1, it may be assumed that these new particles can only be NiAl$_2$O$_4$ particles produced through the solid state reaction. Fig. 4 shows the 60 h milled microstructure and corresponding X-ray mapping images of Al, O and Ni elements. Morphological appearance of these particles is characterized by relatively loose agglomerated spherical shape. In the mapping analysis, it can be seen that all the elements were homogeneously distributed on an atomic scale. As shown in the XRD pattern of the final product (Fig. 1), these elements are in the form of NiAl$_2$O$_4$.

Fig. 5(a) shows a typical TEM image of the product obtained after 60 h milling. In this figure, particles in the range of 5–50 nm with irregular shape and loosely agglomerated feature can be observed. The corresponding SAD pattern of the product in Fig. 5(b) shows a typical ring pattern. This refined structure to nanometer scale is further evinced by the continuous circular SAD pattern. The exhibited rings are assigned to the NiAl$_2$O$_4$ phase which is in agreement with the XRD results.

According to the BET analysis after 60 h milling, specific surface area of the product was 42.3 m^2/g. This high surface area is a relevant feature for good sinterability potential in bulk preparation [21].

3.2. Mechanical activation and heat treatment

In order to complete the characterization of the effect of mechanical activation on the formation of NiAl$_2$O$_4$ spinel, thermal analysis of the initial powder mixture and the 15 h mechanically activated sample was investigated. DTA curves of these samples are shown in Fig. 6. The curve related to the initial powder mixture in Fig. 6(a), shows only a broad endothermic peak between 1020 and 1340 °C. Based on this peak, three initial powder mixtures were heat treated at three temperatures; lower than the onset temperature (900 °C), in the middle (1200 °C) and after the peak (1400 °C). The XRD results of these samples are shown in Fig. 7(a). Increasing temperature from 900 to 1200 °C the NiAl$_2$O$_4$ peaks appeared and finally, at 1400 °C the formation of NiAl$_2$O$_4$ was completed. Hence, the endothermic peak in Fig. 6(a) can be attributed to the formation of NiAl$_2$O$_4$. It should be mentioned that, the reaction temperature range observed is in good agreement with the reported ranges in literature [18,11].

The DTA curve related to the 15 h mechanically milled sample in Fig. 6(b) shows two peaks: one low intensity exothermic peak between 340 and 400 °C, and a broad endothermic peak between 800 and 1060 °C. Hence, in comparison with the DTA curve of
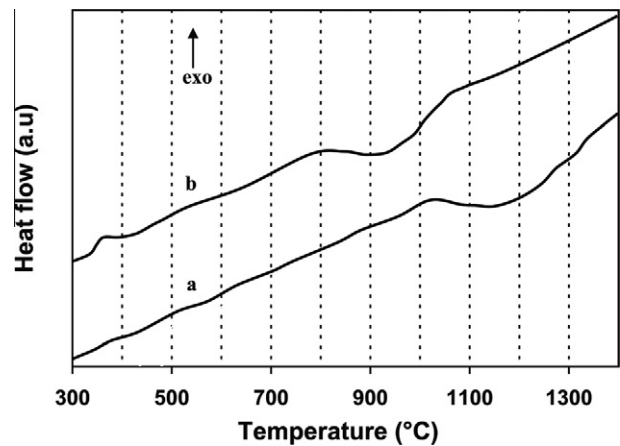

Fig. 6. DTA curves of the (a) initial powder mixture and (b) 15 h milled powder mixture.

initial powder mixture, mechanical activation results in two differences. The first one is the appearance of small exothermic peak at relatively low temperatures and the second one is the shift of the endothermic peak to the lower temperatures. To study these differences in details, effect of heat treatment temperature ranging from 500 to 1100 °C on a 15 h milled sample was investigated. The XRD results obtained after the heat treatment is shown in Fig. 7(b). As it can be seen, increasing the temperature up to 500 °C, no phase change was observed, only the broadening of the peaks was reduced. Therefore, it can be concluded that the small exothermic peak in DTA curve (Fig. 6(b)) appeared due to the release of stored energy from the mechanically alloyed powder via the crystallite size reduction. This is clear that the stored energy in the mechanically alloyed powder is increased by crystallite size reduction and lattice strain increment [16].

The coexistence of NiAl$_2$O$_4$ and the initial constituents' phases in the XRD pattern of heat treated sample at 900 °C suggests that the reaction has not been completed. Raising temperature to 1100 °C completed the formation of NiAl$_2$O$_4$. Therefore, the appearance of the endothermic peak of the 15 h mechanically activated sample was also related to the spinel formation, which shifted to a lower temperature as compared to the non-activated sample. Hence, 15 h of high energy ball milling decreased the temperature of spinel formation at ca. 300 °C. The reason is due to the fact that during 15 h of mechanical activation the diffusivity has facilitated by the creation of the short diffusion paths [16]. In addition, the surface area and surface activity increased as the particle
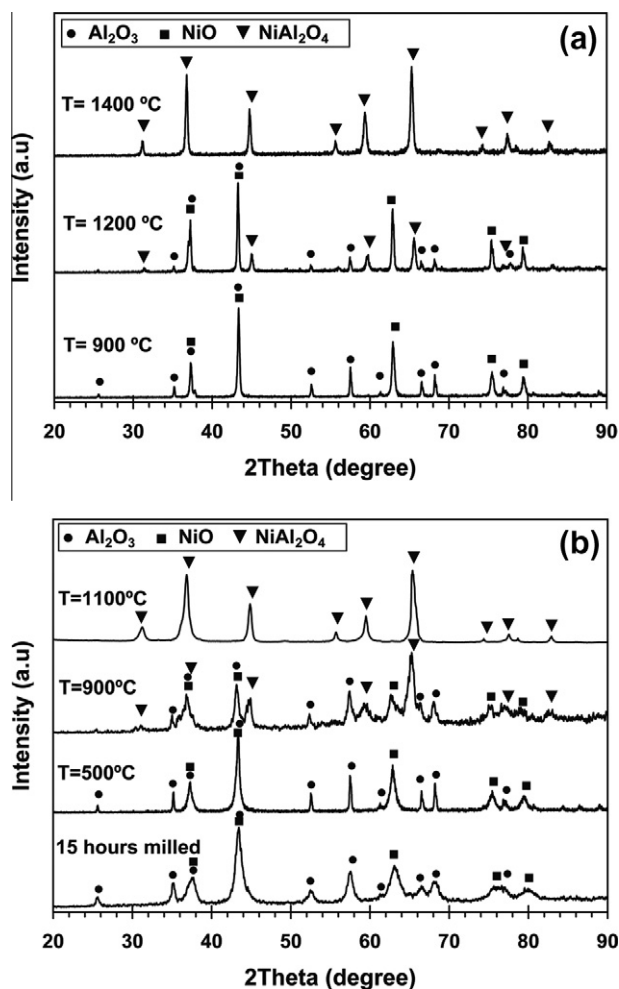
Fig. 7. XRD patterns of (a) initial powder mixture and (b) 15 h milled sample heat treated at various temperatures.

analysis of crystallite sizes that after heat treatment of the milled sample at 1100 °C for 15 h, the average crystallite size was increased from 23 to 57 nm which is still within the nanometer scale. This also implies that during the phase formation, any significant crystallite growth of the spinel particles was not taken place. This is probably due to the fact that the phase transformation inhibits any significant crystallite coarsening.

It is worth noting that one of the shortcomings of the solid state route is that at temperatures around 1200 °C, the residual Al_2O_3 dissolves into spinel structure and forms an Al_2O_3–$NiAl_2O_4$ solid solution, which leads to the excess of NiO in final products [7,18]. Therefore, decreasing the solid state reaction temperature to less than 1100 °C by 15 h mechanical activation eliminates the aforesaid problem.

The TEM image of $NiAl_2O_4$ obtained after the heat treatment of the 15 h milled sample at 1100 °C is shown in Fig. 8(a). In comparison with Fig. 5(a), relatively large agglomerated particles and sintered clusters, smaller than 200 nm, were observed. Fig. 8(b) illustrates the SAD discrete spotty ring pattern of the product. The difference in shape of SAD pattern in Fig. 8(b) and Fig. 5(b) can be attributed to small crystallite growth during the heat treatment process.

After heat treatment of the final product at 1100 °C, BET analysis showed a specific surface area of 5.3 m^2/g. This relatively small surface area can be attributed to the agglomeration and sintering of the particles during heat treatment which was confirmed by TEM results.

4. Conclusions

This study demonstrates the utility of mechano-chemical synthesis for solid state transformation of spent catalysts to a valuable product. The suggested process is particularly cost-effective, where the constituent is formed in a single step. Hence, this route has an industrial significance. This process has the advantage over the other known process for obtaining the nanostructured $NiAl_2O_4$ spinel powder regarding the reaction temperature. Totally, the following conclusions can be made from this work:

(1) XRD and SEM results revealed that solid state reaction of Al_2O_3 with NiO was completed after 60 h milling. After 60 h milling, $NiAl_2O_4$ powder had relatively spherical shape with uniformly distributed elements.
(2) Based on the thermal analysis, the formation of $NiAl_2O_4$ from non-activated mixture was completed at ca. 1340 °C. However, applying 15 h mechanical activation decreased the temperature of spinel formation by ca 300 °C and the com-
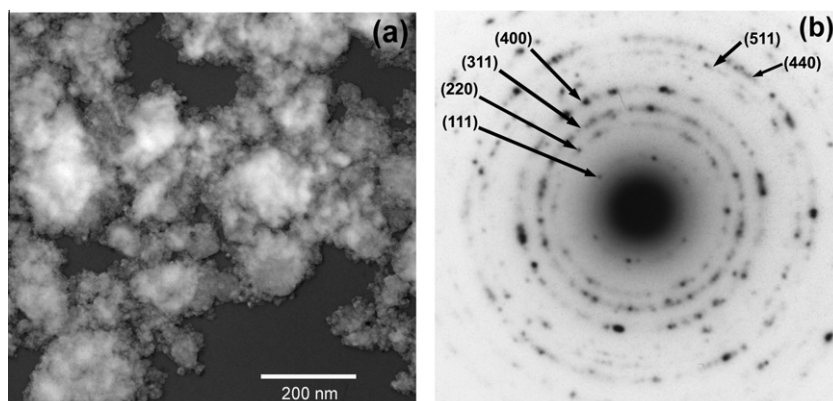
size reduced and concentration of the defects increased. Thus, it is expected that the kinetics of reaction between NiO and Al_2O_3 which is controlled by aluminum ions diffusion becomes faster as compared to the non-activated sample.

The XRD patterns of the 60 h milled sample (Fig. 1) and mechanically activated sample, after heat treatment at 1100 °C (Fig. 7(b)) were found to be very similar. The only significant difference observed was in their peak broadening. It was found from the

Fig. 8. TEM image of $NiAl_2O_4$ after heat treatment of 15 h milled sample at 1100 °C (a) bright field image and (b) SAD pattern.

pletion temperature decreased to 1060 °C. Precursor materials mixing at the nanometer level and increase of surface area and surface activity together with creating short diffusion paths during high energy milling seems to be the key factors allowing spinel formation at a relatively low temperature.

(3) TEM and BET results confirmed the formation of $NiAl_2O_4$ with small particle size and high surface area (42.2781 m^2/g) by direct mechano-chemical synthesis which could not be formed by conventional methods. The crystallite size of the products increased from direct mechano-chemical synthesis route to mechanical activation and consequence heat treatment route.

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