

# Investigation of the Effect of Milling Time on the Mechanochemical Synthesis of Fe<sub>3</sub>Al/ Al<sub>2</sub>O<sub>3</sub> Nanocomposite

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**Abstract**—In this study, the effect of mechanical activation on the synthesis of Fe<sub>3</sub>Al/Al<sub>2</sub>O<sub>3</sub> nanocomposite has been investigated by using mechanochemical method. For this purpose, Aluminum powder and hematite as precursors, with stoichiometric ratio, have been utilized and other effective parameters in milling process were kept constant. Phase formation analysis, crystallite size measurement and lattice strain were studied by X-ray diffraction (XRD) by using Williamson-Hall method as well as microstructure and morphology were explored by Scanning electron microscopy (SEM). Also, Energy-dispersive X-ray spectroscopy (EDX) analysis was used in order to probe the particle distribution. The results showed that after 30-hour milling, the reaction was started, combustibly done and completed.

**Keywords**—hematite, mechanochemical, milling, nanocomposite

## I. INTRODUCTION

THE most prominent characteristic of intermetallic-based composites compared to the monolithic metals and alloys is high specific strength and high modulus that make them ideal materials for structural applications. Iron aluminides are based on Fe<sub>3</sub>Al and FeAl, however, these aluminum-rich phases with melt points about 1150°C are major phases of aluminum alloys [1]-[3]. The most important property of Iron aluminide is high specific strength. The Iron aluminides are the most important engineering materials because of their low cost, low density, high hardness, high melting point and high specific stiffness [4], [5]. Furthermore, these materials possess good wear, corrosion, oxidation and sulfidation resistance. On the other hand, iron aluminides have relatively high electrical resistance and low thermal conductivity. A set of these properties makes them proper materials for many various applications such as structural applications, barrier coatings, hot gas filters, thermal elements, high temperature mould, cutting tools and defense and aerospace industries [6]-[8]. Two major problems, both low ductility at low temperature and unsuitable creep resistance at high temperature about 500 to 600°C, limit the application of iron aluminides. In order to achieve reasonable ductility at room temperature avoiding from stoichiometric compound of FeAl is recommended. When the concentration of aluminum increases, intrinsic defect of grain boundary leads

to brittleness of most of the iron aluminides so that the brittleness of the FeAl at room temperature is higher than Fe<sub>3</sub>Al. Another method is grain size decreasing which results in nanocomposite products [9], [10]. In addition, the ceramic reinforcing particles have been utilized to improve the creep resistance. Principally, second phase particles can be applied in matrix either by ex-situ method such as casting process or by in-situ method [4]. But former method is not proper because of lack of homogenous distribution of reinforcements, pollution creating and low economical efficiency so that the reinforcement particles can be applied in matrix by in-situ and direct method which is occurred by the below substitutional reaction:



Which MO is a metallic oxide which is reduced to a pure metal M or an intermetallic compound by reduction agent R. The in-situ method can be occurred by mechanochemical process [5], [6]. The mechanochemical consists of the mechanical activation of the solid state reactions in a high-energy mill. Primarily, this process had been used by Schaffer and McCormick in the reduction of CuO by Ca [7]. According to reaction adiabatic temperature, the mechanochemical reactions are categorized in two groups. First group has high enthalpy which occurs during the milling process (in fact, the adiabatic temperature of this group of the reactions is higher than 1800K). Second group has low enthalpy and requires subsequent heat treatments (in fact, the adiabatic temperature of this group of reactions is lower than 1800K). The reaction of the first group can be done by either combustion or gradual mechanisms. Recently, the mechanochemical processes have been taken into attention by many researchers and nanocomposites such as NiAl-Al<sub>2</sub>O<sub>3</sub> have been produced [6], [11].

In this research, the effect of mechanical activation time on the synthesis of Fe<sub>3</sub>Al/Al<sub>2</sub>O<sub>3</sub> nanocomposite from hematite and aluminum by mechanochemical process has been studied.

## II. MATERIALS AND RESEARCH METHOD

The precursors consist of commercial aluminum powder (99.9% degree of purity) and hematite powder produced by Merck Company (99.9% degree of purity). The mechanochemical process has been done in planetary mill with weight ratio 1:5 and the rotating speed 250 rpm. According to stoichiometric ratio of related reaction (2), for each stage, powder with 10g weight has been milled under Ar atmosphere without any Process Control Agent (PCA). The phase changes

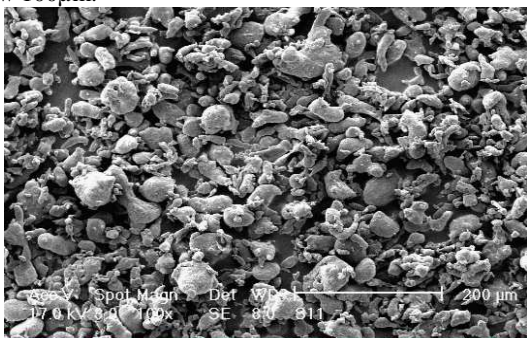
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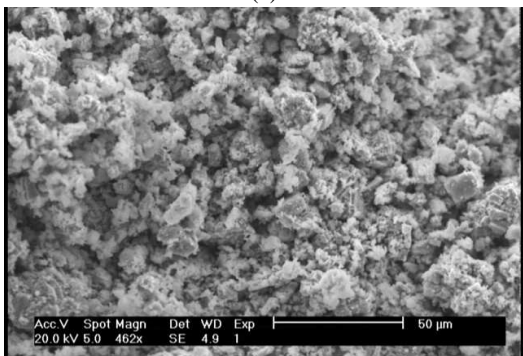
have been investigated by X-ray diffraction (Buroker-D8TOOLS) and the morphology of particles has been explored by Scanning Electron Microscope (Phylips-XL30). In order to probe the elemental compound of powder, the X-ray energy analyzer (Vegal-QUANTANA-QX2) has been utilized. In addition, to investigate the density changes and porosity percentage of powder, the gas pycnometer (Micromeritics) has been used. Also, in order to determine the crystallite sizes and the degree of lattice strain, Williamson-Hall method has been applied.

### III. RESULTS AND DISCUSSION

Fig. 1 shows the morphology of initial Aluminum and hematite powders in which aluminum powder has disorder shaped particles with grain size below 100 $\mu\text{m}$  as well as porous hematite powder has spherical particles with grain size below 100 $\mu\text{m}$ .



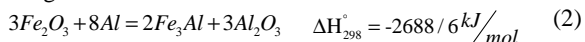
(a)



(b)

Fig. 1 Scanning electron microscope micrographs of initial powders, (a) Aluminum (b) Hematite

In order to produce the  $\text{Fe}_3\text{Al}-\text{Al}_2\text{O}_3$  compound, the precursor materials with stoichiometric ratio have been used according to the below reaction:



$\Delta H$  shows that this reaction is an exothermic reaction and if reaction kinetic is supplied, the occurrence of the reaction will be possible. The adiabatic reaction is a parameter that predicts the state and also presents that how the mechanochemical reaction occurs. The adiabatic temperature of the reaction (2) is measured according to (3):

$$-\Delta H_{298}^\circ = \sum \left[ \int_{298}^{T_m} C_{ps} dT \right] + \sum \Delta H_m^p + \sum \left[ \int_{T_m}^{T_{ad}} C_{pl} dT \right] \quad (3)$$

Which  $C_{ps}$  and  $C_{pl}$  are heat capacity of solid and liquid products, respectively. Also,  $\Delta H_{298}^\circ$  and  $\Delta H_m^p$  are the enthalpy of the reaction (2) and the liquid products, respectively. Thus, the measured adiabatic temperature of the reaction (2) is about 3158K and so that the mechanochemical reaction, which has been done during the milling process, is a combustion reaction. Generally, this type of reaction has spontaneously been occurred and produced during the mechanical activation. Fig. 2 shows the X-ray diffraction pattern of Al and hematite powder mixture before and after the various time periods of the milling process. According to Fig. 2 (b) after 5 hrs of milling of similar initial powder mixture, resulted peaks are compatible with Aluminum and hematite and no other crystal phase has been seen in the vicinity of them. Thus, 5 hrs of milling does not affect on initial powder and only phenomenon, which has been seen, was the decrease of the intensity of initial peaks and the increase of peak width because of nanostructure formation and lattice strain increase. The measured size of crystallite and lattice strain are 66 nm and 0.53% for aluminum and 58nm and 0.925% for hematite, respectively, after 5 hrs of milling. But there is not any precursor after 10 hrs of milling and resulted peaks are compatible with  $\alpha\text{-Al}_2\text{O}_3$  and  $\text{Fe}_3\text{Al}$  according to Fig. 2 (c). Therefore, after 10 hrs, mechanochemical reaction has been done and aluminum has completely been reduced and  $\alpha\text{-Al}_2\text{O}_3$  phase has been formed. However, the materials have been composed of  $\alpha\text{-Al}_2\text{O}_3$  and  $\text{Fe}_3\text{Al}$  by mechanochemical process. The size of crystallite and the degree of lattice strain, which have been measured by Williamson-Hall, have been presented in table I for productions after various milling time. According to this table, the decrease of lattice strain of the sample, which has been milled after 10 hrs, is due to continuous and great striking of the balls to powders during the milling process that results in defect density and localized temperature increase so that the possibility of the diffusion increases that this leads to recovery of the dislocations. The recovery process is carried out by the cross slip [6] of the dislocations so that the degree of the lattice strain decreases slightly.

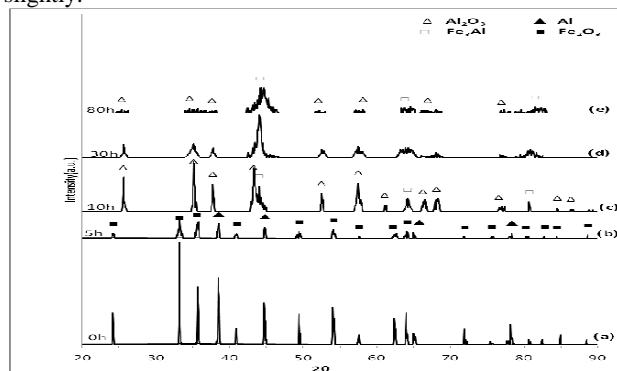


Fig. 2 The x-ray pattern of powder mixture (a) initial, (b) 5-hour, (c) 10-hour, (d) 30-hour and (e) 80-hour milling.

TABLE I  
CRYSTALLITE SIZE AND LATTICE STRAIN OF MILLED SAMPLES AFTER VARIOUS TIME PERIODS

Sample	Crystallite size of Fe <sub>3</sub> Al (nm)	Crystallite Size of $\alpha$ -Al <sub>2</sub> O <sub>3</sub> (nm)	Lattice strain of Fe <sub>3</sub> Al (%)	Lattice strain of $\alpha$ -Al <sub>2</sub> O <sub>3</sub> (%)
10-hour milled	52	73	0.22	0.14
30-hour milled	28	39	1.02	0.65
80-hour milled	11	19	2.76	2.21

According to Fig. 2, if milling process continues up to 30 and 80 hrs, a novel compound will not be formed and if time of milling increases, only peak width will be increased. The reason of this phenomenon can be due to two parameters, crystallite size decrease and lattice strain increase as shown in Table I. Furthermore, the intensity of the related peaks of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase is weak and this is because of the decrease of the crystallites of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase. In addition, the spread of the peaks confirms this issue.

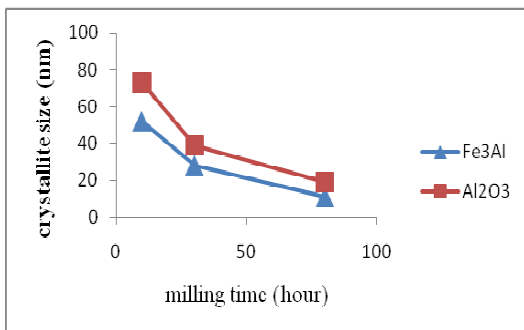


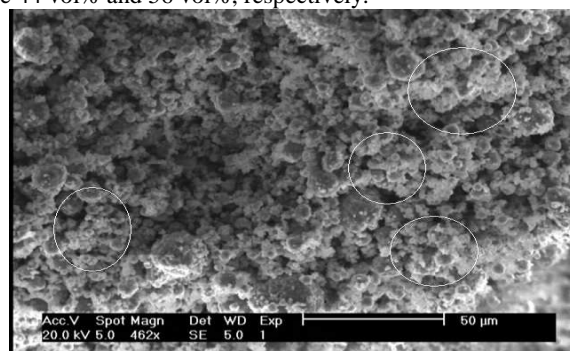
Fig. 3 The size of crystallite (nm) versus milling time (h)

Fig. 3 illustrates the variation of the crystallite size versus the time of milling. According to Fig. 3, when the milling time increases from 10 hrs to 30 hrs, the decrease of the crystallite size is happened more rapidly than that when the milling time increases from 30 hrs to 80 hrs. The reason is when the milling time increases, cold coherence phenomena and consecutive fracture will be occurred and then the equilibrium will be achieved. Thus, the decrease rate of the crystallite size will decrease.

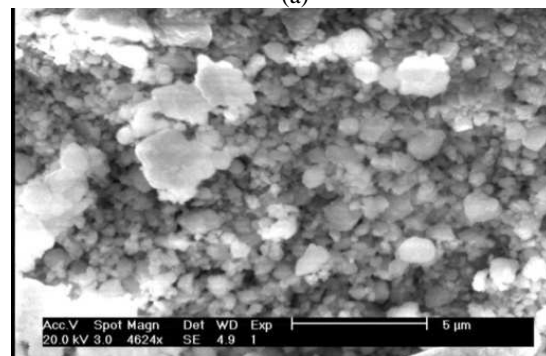
Fig. 4 (a) shows the morphology of the powder particles after 10-hour milling. The morphology of particles is porous and the average size is about 20  $\mu$ m. The porosity percentage achieved by gas pycnometer is 26% that presents the high porosity of powder and meets the morphology of the porous powder in which the morphology of the porous powder particle can be due to the combustion reaction of the mechanochemical reaction.

Fig. 4 (b, c) illustrates the morphology of the powder particles after 30 and 80-hour milling. Because of 30-hour milling, the size of the resulted phase particles decreases and reaches to 5  $\mu$ m and the porous morphology has not significantly been seen and also the decrease of the porosity percentage to 8.37% confirms this issue. If milling process continues to 80 hrs, the size of the particles will decrease to about 1  $\mu$ m. While the powder particles agglomerates and the porosity percentage increases compared to that of 30-hour

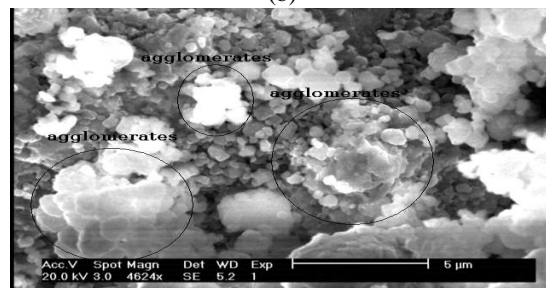
milled counterpart and reaches to 10.17%. The agglomeration of the particle in 80-hour milled sample is due to that decreasing the particles leads to attach each other. Because of the presence and the formation of the brittle compound of alumina and iron aluminide, according to Fig. 4, if the milling process goes on, they will be fractured so that this phenomenon will make the distribution of the powder particles better and more homogenous. According to Fig. 5 that shows the linear distribution of the elements in 30-hour milled sample, the distribution of the elements is uniform and homogenous. In addition, the coincidence of the oxygen and aluminum peaks and also the presence of the average percentage of the aluminum and iron throughout the path present the Fe<sub>3</sub>Al and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase existence. Fig. 6 indicates the point scan analysis of the 30-hour milled sample. According to Fig. 6, the volume fraction of Fe<sub>3</sub>Al and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are 44 vol% and 56 vol%, respectively.



(a)



(b)



(c)

Fig. 4 Scanning electron microscope micrograph of aluminum and hematite powder mixture after (a) 10-hour, (b) 30-hour and (c) 80-hour milling

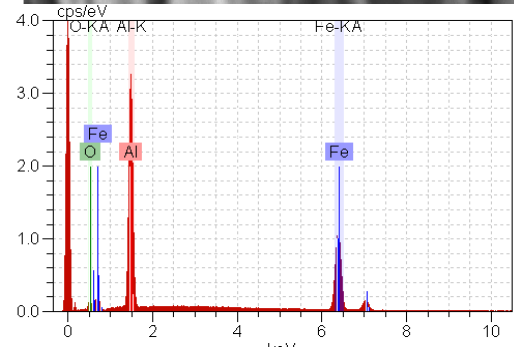
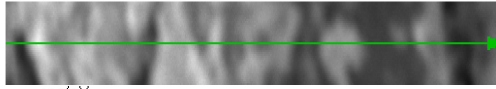
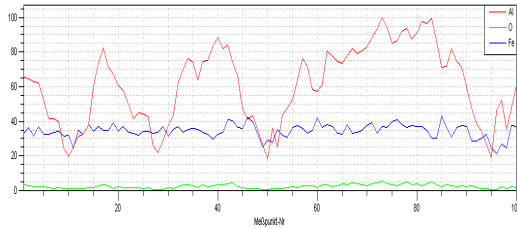
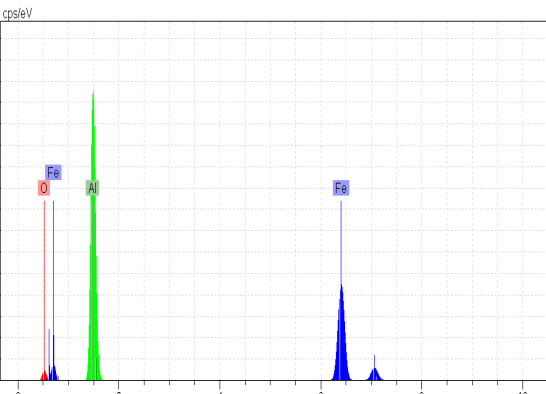


Fig. 5 Linear scan analysis of the 30-hour milled sample



Element	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]
Oxygen	K series	1.21	1.24	2.97
Aluminum	K series	38.96	39.93	56.68
Iron	K series	57.41	58.83	40.35
Total:		97.6 %		

Fig. 6 Point scan analysis of the 30-hour milled sample

IV. CONCLUSION

The results indicate that mechanochemical reaction of aluminum with hematite has been done and completed by milling process after 10 hrs. This phenomenon presents a combustion reaction and the method which can directly produce Fe<sub>3</sub>Al-Al<sub>2</sub>O<sub>3</sub> nanocomposite. This nanocomposite consists of 44 vol% alumina phase. If the milling process continues, the crystallite size will only decrease and result in homogenous distribution of phases in the nanocompoiste.

REFERENCES

- [1] M. Krasnowski, T. Kulik, "Nanocrystalline FeAl Matrix Composites Reinforced with TiC Obtained by Hot-Pressing Consolidation of Mechanically Alloyed Powders", *Intermetallics* 15, 2007, pp. 1377-1383.
- [2] M. Krasnowski, A. Witek, T. Kulik, "The FeAl-30%TiC Nanocomposite Produced by Mechanical Alloying and Hot-Pressing Consolidation", *Intermetallics* 10, 2002, pp. 371-376.
- [3] M. Krasnowski, T. Kulik, "FeAl-TiN Nanocomposite Produced by Reactive Ball Milling and Hot-Pressing Consolidation", *Scripta Mater.* 48, 2003, pp. 1489-1494.
- [4] M. Rafiei, M.H. Enayati, F. Karimzadeh, "Mechanochemical Synthesis of (Fe,Ti)<sub>3</sub>Al-Al<sub>2</sub>O<sub>3</sub> Nanocomposite", *J. Alloys Compd.* 488, 2009, pp. 144-147.
- [5] M. Khodaei, M.H. Enayati, F. Karimzadeh, "The Structure and Mechanical Properties of Fe<sub>3</sub>Al-30vol.%Al<sub>2</sub>O<sub>3</sub> Nanocomposite", *J. Alloys Compd.* 488, 2009, pp. 134-137.
- [6] M. Khodaei, M.H. Enayati, F. Karimzadeh, "Mechanochemically Synthesized Fe<sub>3</sub>Al-Al<sub>2</sub>O<sub>3</sub> Nanocomposite", *J. Alloys Compd.* 467, 2009, pp. 159-162.
- [7] M. Rafiei, M.H. Enayati, F. Karimzadeh, "Characterization and Formation Mechanism of Nanocrystalline (Fe,Ti)<sub>3</sub>Al Intermetallic Compound Prepared by Mechanical Alloying", *J. Alloys Compd.* 480, 2009, pp. 392-396.
- [8] M. Krasnowski, T. Kulik, "Nanocrystalline FeAl Intermetallic Produced by Mechanical Alloying Followed by Hot-Pressing consolidation", *Intermetallics* 15, 2007, pp.201-205.
- [9] L.M. Peng, H. Li, J.H. Wang, M. Gong, "High Strength and High Fracture Toughness Ceramic-Iron Aluminide (Fe<sub>3</sub>Al) Composites", *Mater Lett.* 60, 2006, pp. 883-887.
- [10] D.G. Morris, M.A. Munoz-Morris, J. Chao, "Development of High Strength, High Ductility and High Creep Resistant Iron Aluminide", *Intermetallics* 12, 2004, pp. 821-826.
- [11] S.Z. Anvari, F. Karimzadeh, M.H. Enayati, "Synthesis and Characterization of NiAl-Al<sub>2</sub>O<sub>3</sub> Nanocomposite Powder by Mechanical Alloying", *J. Alloys Compd.* 477, 2009, pp. 178-181.