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SOLID-STATE REACTION IN Al-Fe BINARY SYSTEM INDUCED BY MECHANICAL ALLOYING

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Abstract

Mechanical alloying (MA) is a solid-state powder processing method which has the ability to synthesize a variety of new alloy phases including supersaturated solid solutions, nanocrystalline structures, amorphous phases and intermetallic compounds.
In this investigation, the interaction between aluminum and iron caused by MA of Fe-XAl (where X ranged between 30 to 90%) has studied as a function of milling time post heat-treating temperatures. The sequences of structural and/or phase transformation and the behavior of mechanically alloyed powders have been assessed using XRD, hardness and magnetometer.
It was found that, during mechanical milling of element powder Al and Fe, five milling stages can be categorized, namely, particle flattening, welding predominance, equiaxed formation, random welding orientation and steady state composite particles. All milled powders showed nano-sized powder mixtures after milling for 20hrs. When Fe-30Al powder was milled for 150hrs, partially ordered AlFe phase was obtained. However, when these saturated solid solutions were heat treated at 500^0C, AlFe intermetallic was precipitated in fully ordered. When the Al increasing up to 40% and milled for 50hrs, the XRD pattern showed a broad halo, for solvent spectrum which mst formation of an amorphous phase. When Fe-60%Al powder mixture was mechanically milled Al_5Fe_2 intermetallic formed associated with an amorphous phase, which transformed into Al_3Fe intermetallic by heat treating at500^0C.In case Fe-75%Al an Fe-90%Al milled for 150hrs only Al peaks abroad and were shifted to higher angles, suggesting that Fe atoms diffused into Al, leading to the formation of a solid solution.

KEY WORDS: Mechanical alloying, Al-Fe, intermetallic and Magnetic Properties

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1. Introduction

Intermetallic aluminides exhibit low density, high melting points, good thermal conductivity, good oxidation behavior and superb high-hemperature-strength [1]. As a result, many of these intermetallics are particularly suited for structural applications at elevated temperatures [2]. Mechanical alloying (MA), a solid state powder processing technique, has been employed to synthesize a variety of alloy phases from either blended elemental or prealloyed powders [3,4]. The repeated welding, fracturing and rewelding of powder particles can lead to the formation of supersaturated solid solutions, crystalline and quasicrystalline intermediate phases, and metallic glasses [3, 4]. Recently there have been many investigations on the synthesis of intermetallic compounds by MA [5]. However, the synthesis of most the intermetallics is achieved only on heat treatment of the MA powders. The formation of the intermetallics is seldom to be achieved directly by MA [6, 7]. The selection of the (Fe-Al) binary system is based on the following considerations. First of all, there are many different phase transformations, which require different stages of ordering, exhibit attractive elevated temperature of strength, stiffness and environmental resistance. Second, some alloying between Fe and Al forming amorphous materials by either milling or rapid solidification has been reported in some recent publications [8-10]. In addition, partially ordered nanocrystalline powders formed from Fe and Al was already obtained after long period of milling [11].
In this paper, the interaction between aluminum and iron caused by MA of Fe-XAl where X ranged [30, 40, 60, 75 and 90] has been studied as a function of milling time post heat-treating temperatures in addition some physical properties have been measured.

2. Experimental

Raw materials used were high pure powders of Fe and Al at least 99.9% purity. The powder sizes were smaller than 45μm. These powders were blended to form composition of (Fe-XAl) alloys, where X is ranging [30, 40, 60, 75 and 90] in order to cover almost all main compositions of the binary systems of (Fe-Al).
A home-made shaker-type mill was used for mechanical milling. The shaker mill has one vial made from high Cr-steel of inner diameter of 75mm, length of 120mm, and grinding balls made from hardened steel of 6mm diameter. The vial rotates around its length axis and shake up and down combined with lateral movements of the ends of the via. The rotation speed is 180rpm, and the up and down swing of the vial is 360 time/min. The amplitude of the vial swing is 30MMc. The mechanical alloying process was carried out at roam temperature and in argon atmosphere.
Hardness tests were performed for as milled powders. The powders were mounted in a cold epoxy resin cured at room temperature and were successively polished by diamoned paste down to 0.25μm. Microharness data of the milled powders were measured by an indentation technique, using Vickers Hardness Tester type (Shimadzu Microhardness), at a load of 25gm. About eight to ten measurements were made on each sample.
A philips X-Ray diffract meter (XRD), type PW1370 was used to examine the structure variation during milling, at 30kV potential and 25mA current at scanning speed of one (cm) 2θ per minute. From XRD patterns, the average grain size of the

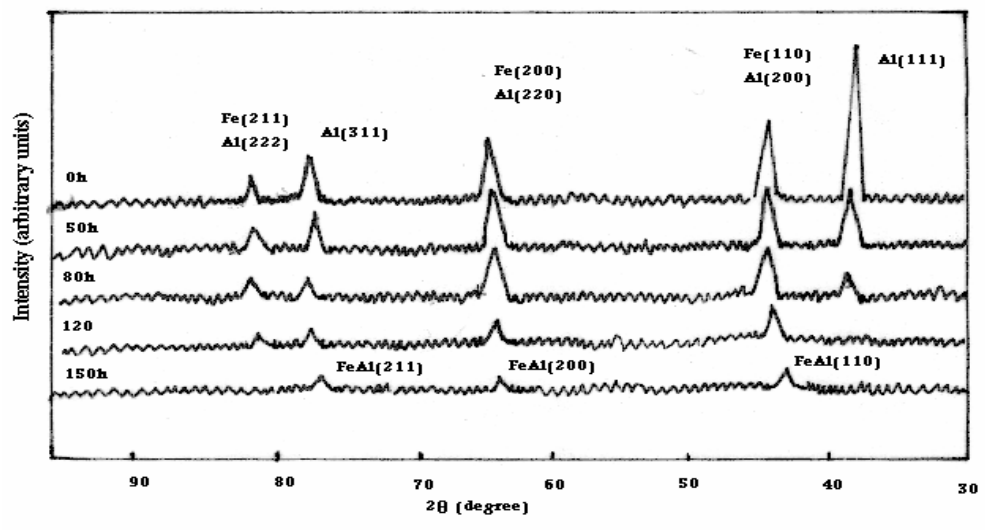
formed phases was calculated from the full width at half-maximum of main peak measurments, using the Scherrer`s equation [10]. The lattice parameter (a0) was determined for the milled powder by XRD using internal standerd as mentioned by Klug and Alexander [11]. The magnetic measurements are realized using a hystereimeter LDJ Electronics, Inc Troy, MT U.S.A 9600-1 VSM.

3. Results and Discussion:

3.1 XRD Analysis:

The XRD was used to follow the structural changes during mechanical alloying of (Fe-XAl) powder mixtures, and to measure the changes in crystallite size, lattice parameter and strain as a function of milling time. Fig.1 (a) shows XRD patterns of Fe-30% Al alloy as a function of milling time. The as powder mixture, showed all the expected peaks from both Fe and Al, with the Fe (110), Fe (200) and Fe (211) peaks overlapping with the Al (200), Al (220) and Al (222) peaks, respectively. As milling time increased, the extent of diffusion of elemental Fe into Al during milling leading to the formation of FeAl, where the disappearance of the Al peak is evident after about 120 hr milling. Longer milling times up to 150 hr leave the alloyed powders in a partially ordered state. The lattice parameter of FeAl, calculated from Fe (110), had increased from the initial value of 0.2866nm, in the blended stat, up to 0.2885nm, after milling time of 120hr, which remained constant with increasing milling time up to 150hr, indicating that the maximum solubility level had been reached. The crystallite size was calculated for each alloy from the broadening of X-ray peaks at half width of main peak using the Scherrer formula [12]. Fig. 2 shows the variation of crystalline size with milling time, from which it can notice that nanometer- sized crystals were formed after long milling. Also, the average root mean square rms - strain of Fe-30%Al increased with the increase of milling time, see Fig.3. This might be due to the introduction of excessive cold working into the powder particles due to milling effect, which resulted in the generation of high saturation of defects producing high strains. When Fe-40%Al powder mixture was mechanically milled, it was found that the resultant structure up to 120hr was similar to that of Fe-30%Al. However, with increased milling time to 150hr, the XRD pattern showed a broad halo, suggesting the formation of an amorphous phase, as indicated in Fig. 1 (b). If the Fe content was increased such that the initial composition of the powder mixture was Fe-60%Al, Al5Fe2 intermetallic started to form after 120hr milling time, with presence of amorphous phase at 2θ 400 to 450, as indicated in Fig.1 (c).
Fig. 1(d) shows the XRD patterns of Fe-75%Al powder mixture as a function of milling time. No evidence of formation of Al3Fe phase can be detected even after 150hr of mechanical milling, and
Only Al solid solution was observed. There are two possibilities for this lack of formation: 1. no formation of Al3Fe phase with this composition after 150hr of mechanical alloying, or 2. formation of Al3Fe phase but in the nanocrystalline form. The XRD patterns of Fe-90%Al powder as a function of milling time is shown in Fig. 1 (e). With increasing milling time, the Al peaks shifted to higher angles, suggesting alloying of Fe into Al, leading to the formation of a solid solution. Again there is no evidence for the presence of Al3Fe can be detected even after mechanical alloying for 150hr. The two possibilities that have been mentioned above are also applied for this case.

The mechanical alloying process of Fe-XAl mixed powder passed with five stages, namely, particle flatting, welding between particles, equiaxed particle formation random welding orientation, and steady state [13-14]. During these stages, there is a competition between the fracturing and cold welding mechanisms. Consequently, depending on the dominant forces, a particle many either become smaller in size through fracturing or many agglomerated by welding. At steady state stage, a balance is achieved between the amount of welding and the amount of fracturing. Considerable refinement and reduction in particle size is observed in this stage.



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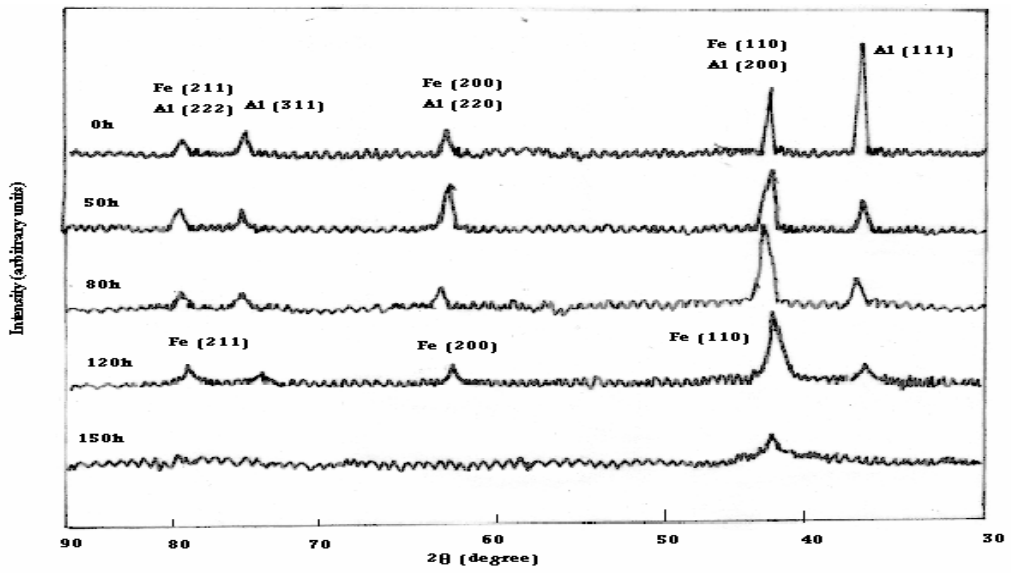

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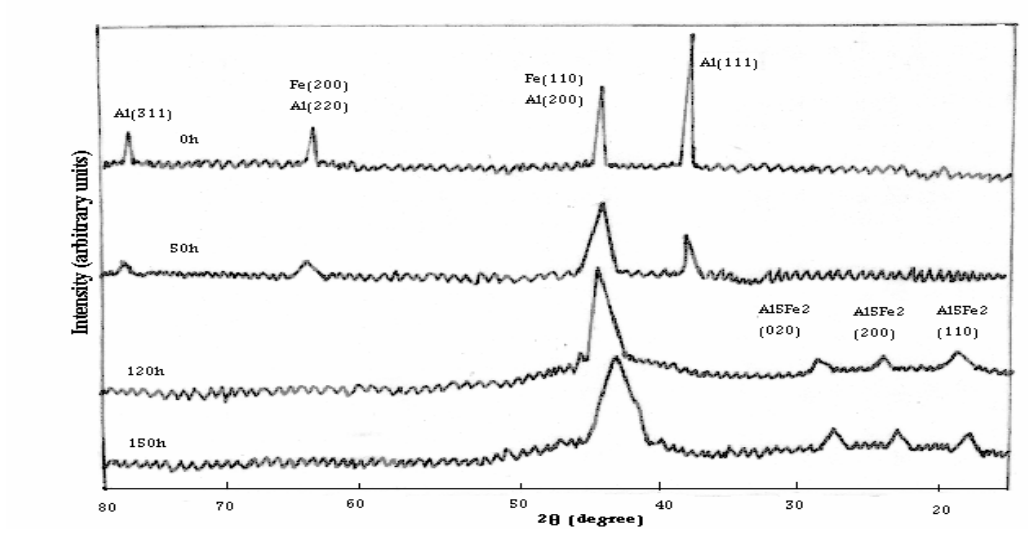

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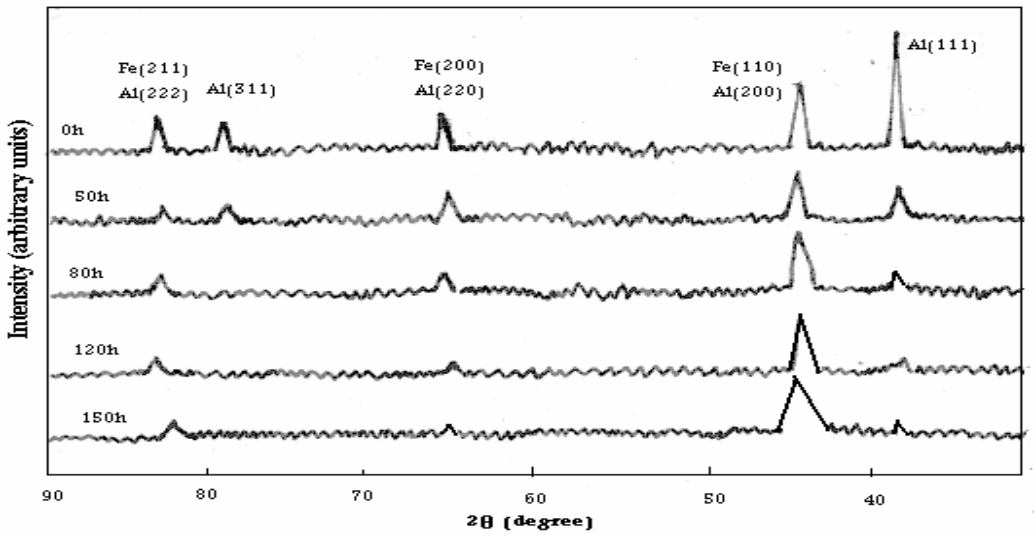

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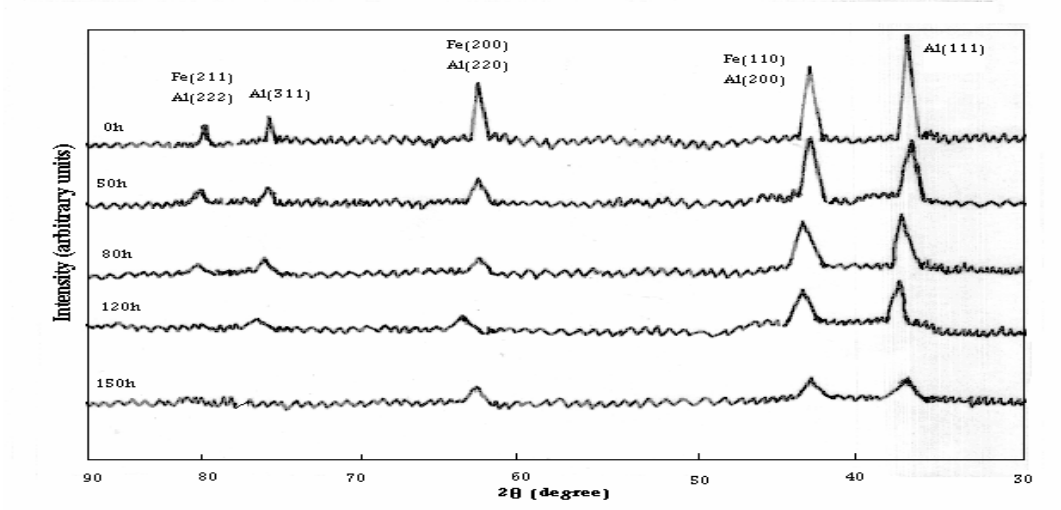


e

Fig 1. XRD patterns of powders milled for different time, a-Fe-30%Al, b-Fe-40%Al, c-Fe-60%Al, d-Fe-75%Al, e-Fe-90%Al.

All the lamellae of different particles (i.e. Al and Fe) with the powder particle have reduced to a thickness less than a wavelength, which means very high surface areas of contacted and high stressed elements are formed leading to high diffusion rate between these lamellae.
The cycling effect of fracturing and welding mechanisms at this stage induced high strain on these lamellae leading to the formation of either meta-stable or stable phase.
The, grain size strain and the lattice parameter of the various phases are illustrated in Figs 2,3 and 4, respectively. Also, it is observed that the crystallite sizes of all the investigated powder mixtures decreased with very high rate of reduction to nanosized crystals after milling for 50hr, Fig2, and with a lower rate of reduction furtheron. For all phases, it was found that the rms-strain increased with the increase of milling time Fig 3. This might be attributed to the extreme cold working induced into the powders during mechanical alloying. It is noticed that the lattice parameter of Fe-30, 40 and 60%Al were increased with the increase of milling time, whereas those of Fe-75 and 90%Al decreased with the increased time of mechanical alloying.

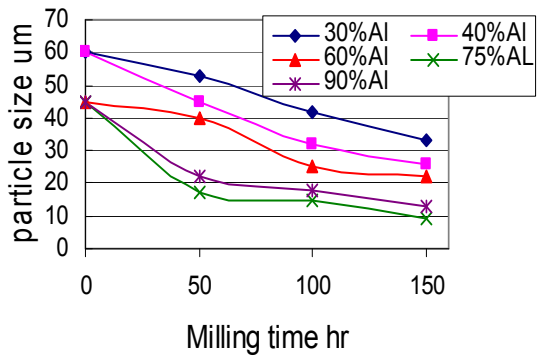


Fig 2. The effect of milling time on particle size.

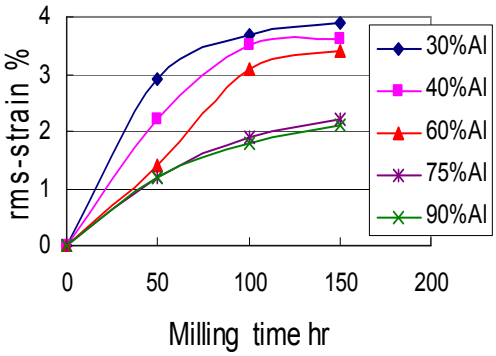
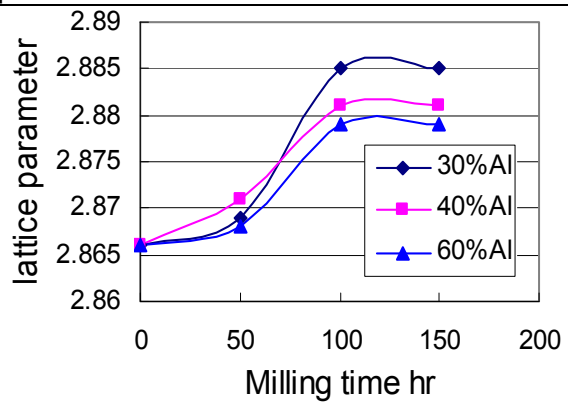
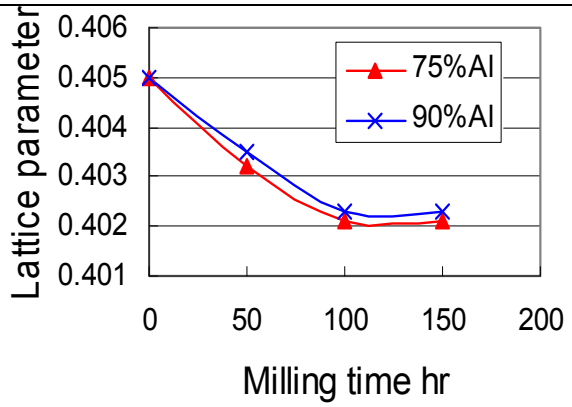


Fig 3. the effect of milling time on rms-strain



a- Lattice parameter of Fe



b- Lattice parameter of Al

Fig 4. The effect of milling time on lattice parameter.

3.2 Hardness Measurements of (Fe-Al) Powders:

Hardness measurement is considered very useful tool for monitoring the degree of any structural or morphological changes in a material due to one or more of the following: 1. Induced strain due to cold working, 2. Stress- relieve due to recovery

and recrystallization, 3. Precipitation or decomposition of a phase or phases, and 4. Grain-growth. It was used in this investigation for studying the progressive plastic deformation on investigated powders during mechanical alloying and hence understanding the different alloying mechanisms involved during the mechanical alloying process.

Fig 5 shows the relation between microhardness of milled powders and the milling time for Fe-30, 40, 60, 75 and 90%Al powder particles. First of all, it is observed that there is a decrease of hardness values with the increase of Al content for all starting powder mixtures. The measured hardness value was the mean values of the measured hardness of both Fe and Al particle at ratios as those of chemical composition. For example, in case of Fe-30%Al powders, the measured hardness value was the mean value of seven measuring hardness values for iron and three measuring values for Al powders. This is attributed to the higher hardness of iron particles compared with that of Al. After short time of milling (about 2hrs.), the "kneading" action of milling led to a continual refinement of internal structure of the metal powders to the extent that individual particle of Fe or Al cannot be identified. Accordingly, any measured hardness value represented the hardness of their composite. Increasing milling time caused the continuous increasing of the hardness of all powder mixtures; however, the rate of increasing depends on the powder mixture composition.

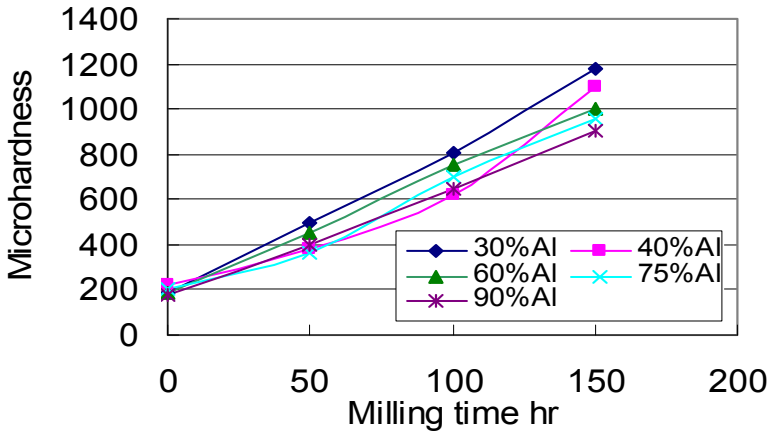


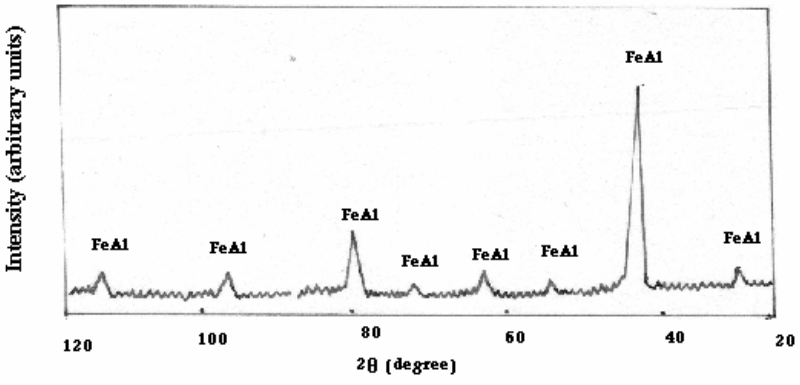
Fig 5. The effect of milling time and composition on microhardness.

Fig. 1, 30Al show a continuous increase of hardness of Fe-30Al powders with milling time up to 100 hr, after which higher of increase is observed, probably due to formation of the intermediate phase FeAl. By increasing Al content up to 40%, the hardness of powders increased with milling time up to 100 hr, and then higher rate of increase was detected further on; see Fig.1, 40Al. This higher rate of increase in hardness after milling time of 100hr could be due to the formation of hard phase either amorphous or intermetallic phase. Almost the same behavior of hardness against milling time was observed for Fe-60% Al powders except that the rate of increasing in hardness was much higher, which could be due to the formation of larger amount of hard phase than that formed in Fe-40%Al, Fig.1, 60Al illustrates the continuous increase of hardness vs. milling time for Fe-60%Al powders. Increasing Al content up to 75%, continuous increase in hardness was observed, but with different rate. Higher rate of increasing in hardness value was observed after milling time of

50 hr; see Fig.1, 75Al. This might be due to formation of hard phase. It is worth noting that the lowest recorded hardness value was belonging to Fe-90% Al and this observation maintained for all milling times, as illustrated in Figs.1, 90Al. This is probably due to the formation of Al FCC solid solution.

3.3 Synthesis OF Intermetallic:

Intermetalic compounds generally have very high melting temperatures and therefore can potentially be used for high- temperature applications but they are brittle at ambient temperature. It has been reported that nanostructured materials have improved ductility over their course- grained counterpart [15]. Many investigators mentioned that intermetallics are not achieved directly by mechanical alloying; rather, a subsequent annealing is required [16]. However, there are some reports of synthesis of intermetallic compounds directly by milling [17-19].
In this study, it has been shown that some intermetallics have been formed directly by mechanical alloying, however, in a partially ordered state or with distorted structure.
In order to evaluate the stability of the phases formed by mechanical alloying, two milled alloys, namely, Fe-30%Al and Fe-90%Al, were heat-treated at 500^0C. The former alloy was chosen to study the effect of annealing on ordering FeAl alloy, whereas the later alloy was chosen to determine whether or not the Al_3Fe will be formed by annealing. Fig.(6) a shows the XRD patterns of the Fe-30%Al powder milled for 150 hr and heat- treated at 700^0C for 5hrs. Sharp XRD peaks are observed with appearance of all the respective peaks corresponding to FeAl phase, suggesting the formation of fully ordered FeAl phase. Morris et.al [20] reported that the mechanism of fully ordered FeAl alloy is by atomic-scale interchange and the movement of defects.
The XRD pattern of the Fe-60%Al powder milled for 150hr and heat treated at 500^0C for 5hrs is shown in Fig.6 (b). It is seen that both Al and Al_3Fe are in evidence after annealing. It has been indicated previously that Al_3Fe could not directly synthesis by mechanical alloying at this composition or at Fe-75%Al alloy, after milling up to 150hr, while Al_5Fe_2 was directly formed by milling action, although the enthalpy of formation of Al_3Fe (28.1 kJ/g.atom) is very close to that of Al_5Fe_2 (28.3 kJ/g.atom). This could be due to the complex crystal (monoclinic) structure and large unit cell.
Dunlap et.al [21] has reported that an amorphous (instead of Al_3Fe) should form in the composition range of Fe-30%Al to Fe-60%Al in the Fe-Al system, which is in agreement with the present study. The intermetallic Al_3Fe could be synthesized with lower Fe contents only after heat- treating the milled powders.



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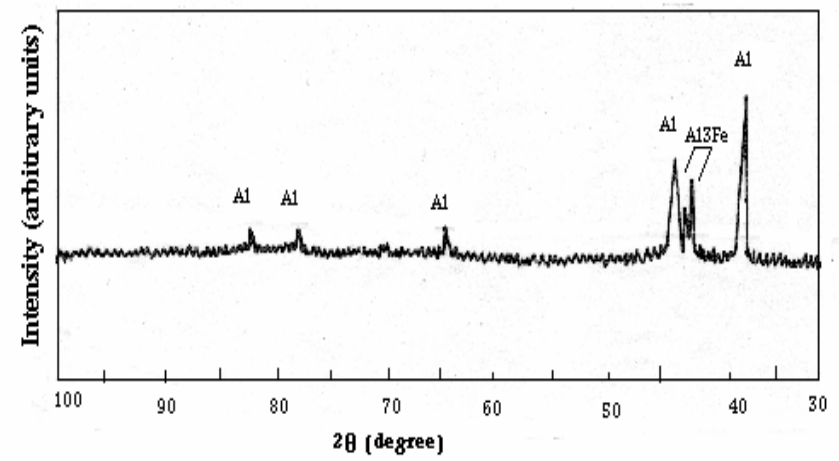

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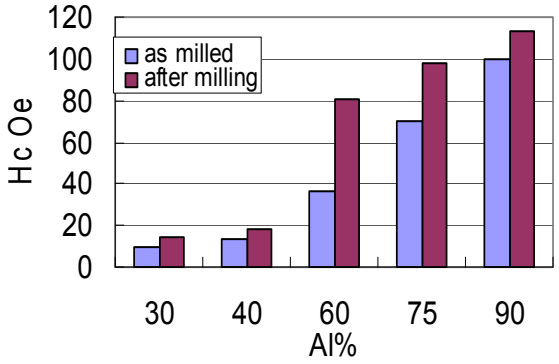
Fig 6. XRD pattern for a-30Al and b-60Al milled for 150 hr an after annealing at 500^0C for 5hr

3.4 Magnetic Properties

The Fe-Al system is of interest because of potential commercial materials of these alloys as structural or magnetic materials. In the Fe rich side of the phase diagram the Fe–Al system has a range of disordered body-centered-cubic (bcc) structures up to 22 at.% Al at room temperature; on increasing the Al content the phase diagram has a variety of intermetallic phases [22] such as Fe_3Al,FeAl,$Fe_{13}Al$… Starting with Al dissolved in Fe the first stable compound is Fe_3 Al with cubic structure and it exists over the 18–37 at.% Al range [23]. The other stable compound is FeAl which is also cubic and it exists over the range 37–50 at.% Al [23].
It has been shown that these alloys are of the ferromagnetic disordered type (bcc) for Al composition up to 22 at.% . At the Al richest compositions the alloy is paramagnetic at room temperature [24].
From this result we can show the effect of the grain size in the coercivity consequence the milling process and the effect of milling in the saturation magnetization.

Table 1: the relation between the composition, milling effect and coercivity, saturation magnetization

Composition		30%Al	40%Al	60%Al	75%Al	90%Al
H_C Oe	As mix	9.5	13.5	36.55	70.5	99.99
	after milling	14.7	18.6	80.3	97.5	113.2
B_S emu/g	As mix	175.3	92.56	55.16	36.67	29.7
	after milling	60.6	80.61	22.31	34.08	26.13



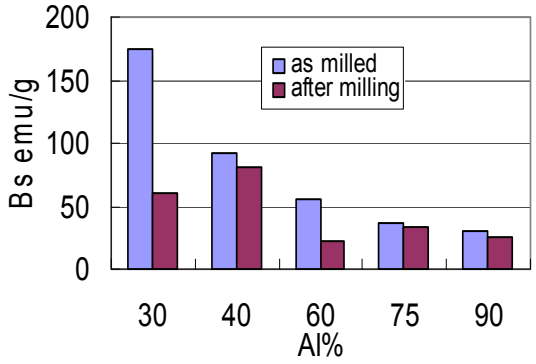


Fig 7. The effect of composition and milling process on coercivity and saturation magnetization

From table (1), According to the decreasing particle size (due to milling), a distinct magnetic hardening process takes place on milling. The coercivity increase after milling.

The saturation magnetization (B_S) decreases after milling due to formation of disorder and amorphous phases in case 40, 75 and 90% Al. In case 30 and 60% Al the lowering in B_S is very high due to intermetallic formation. From table 1 up to 30%Al the system consider ferromagnetic and after these percent the systems consider paramagnetic.

4. Conclusions

1- Nano-meter crystal size can be obtained by mechanical alloying in all investigated (Fe-Al) powder mixture compositions.
2- The partially ordered FeAl phase could be obtained directly by mechanical alloying in Fe- 30 and 40 wt%Al.
3- The Al_5Fe_2 phase could be synthesized directly by milling Fe-60 wr% Al powders
4- Heat treatment of milled powders is necessary to synthesize the Al_3Fe intermetallics and the formation of fully ordered FeAl phase.
5- The coercivity of particles increase for smaller particles.
6- The saturation magnetization of sample decreases after milling due to change in crystal structure.
7- The rate of decreasing in saturation magnetization is higher in case 30Al and 60Al due to intermatallic (Al_3Fe and FeAl) formation

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