Structural Study of Mechanically milled nanocrystalline Fe_{1-x}Al_xalloys using XRD

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Abstract: In this work, the $Fe_{1,x}Al_x$ ($0.3 \le x \le 0.6$) samples were synthesized by mechanical alloying (MA) in a high-energy ball mill under argon atmosphere and then structural properties of these MA alloyed powders were assessed by means of X-ray diffraction (XRD) characterization technique. All the samples were milled for a fixed period of 5 hrs. The phase transformation, structural changes and changes in micro structural parameters such as average crystallite size and lattice constant (a_o) of each sample were examined by XRD. After 5 hrs of milling average crystallite size of about 8nm was obtained. The crystal structure (B2) of bulk as well as of milled samples came out to be same and expansion in lattice strain was observed after alloying of elemental powders. The evolution of micro-structure and disorder in the system was also traced by XRD.

Keywords: Intermetallics, FeAl, Phase formation, Mechanical alloying, XRD.

1. Introduction

Intermetallic compounds which are based on iron aluminides have become most interesting materials for research and development due to their unique size and useful physical, mechanical and thermal properties which are low density, high hardness, resistance to corrosion, oxidation and carbonization, high specific strength at intermediate temperatures, low cost, and high reactance at high temperatures [1]-[9]. The nanocrystallization of materials increases the surface to volume ratio which has significant effect on their properties and introduces interesting properties which also make nanomaterials an interesting material for research and development. The increase in the concentration of Al in the FeAl alloys leads to increase in oxidation and sulphidization of the FeAl alloys but it also causes decrease of their densities [10]. These alloys could be used as a substitute for stainless steel and Ni based alloys due to the improvement in their physical as well as mechanical properties [1], [2], [7], [8]. The properties of FeAl alloys which are mentioned above have made these alloys useful materials for many applications like pharmaceutics, heating elements, high-power magnets, fabric and paper cutting tools, turbochargers, as contacts and interconnections in microelectronics, low cost sensor devices, drug delivery and low cost flat panel displays [4,11]. However, the applications of these intermetallic alloys have been limited due to their drawbacks such as low ductility at intermediate temperature and decrease in their strength at high temperature (6000 C) and hydrogen embrittlement etc [12], 13]. There is a need of improving the mechanical properties of these intermetallic compounds by reducing their size to nanometer in a well systematic way. Therefore, many approaches were used to reduce their imperfections and also to improve their properties such as strengthening of grain boundary, refinement of grain size and oxide dispersion strengthening [4, 5, 7, 9]. Due to the above mentioned factors the study of intermetallic systems has been attracting the interest of scientists and researchers and so many Fe-Al systems of different compositions have been examined in recent years. Another reason for it is that the drawbacks of these materials can be improved, for instance creep resistance can be improved by reinforced particulates and ductility can be enhanced by the refined microstructure.

Various methods have been used to synthesize intermetallic compounds of nanoscale such as casting, gas atomization, mechanical alloying, sintering, and combustion synthesis etc. But MA is the most common technique for the synthesis of intermetallic alloys due to its many beneficial properties i.e. reliable, cheap, high flexiblility in the selection of synthesis processes and different types of products can be attained, simplicity, easy to operate and capable of synthesizing explosive materials etc [4], [5], [8], [9]. When ordered intermetallic alloys were subjected to ball milling, structure of the intermetallic alloys changed in three ways that were nanocrystallization, loss of long range order (LRO), and destruction of chemical short range order.

FeAl alloys have been studied from the past few decades using various techniques due to their advantageous magnetic and structural properties and undeveloped future applications. The type of structures and phases formed are very sensitive to the Fe to Al content. Iron- aluminum phase diagram [14] exhibits several intermetallic phases at varying compositions and temperatures, two ordered phases, namely the B2 and DO₃ pre-dominate the field with stability over a wide range of composition. However use of a nonequilibrium process like mechanical alloying results in the formation of intermediate magnetic phases. Along with nanostructuring and disordering, the presence of these intermediate phases would lead to interesting bulk and microscopic magnetic properties [15]. Both from the point of view of understanding the collective behavior of the magnetic phases and also possible applications, study of such intermediate phases is expected to be very rewarding. With this objective, in order to understand the plethora of often different results and explain in terms of possible inhomogeneities in the system, we have systematically studied the structural evolution of Fe-Al powders mixed in the different compositions by high energy MA treatment for 5 hrs.

2. Experimental Details

The intermetallic Fe_{1-x}Al_x alloys of different compositions, where the value of x varies from 0.3 to 0.6, were prepared by MA of high energy rate ball milling of analytical grade Fe and Al powders of approximately 300 mesh sizes with purity of about 99.9%. The powders were initially mixed thoroughly using agate pestle and mortar and then to prevent them from oxidation phenomena each powder sample wasdry-milled in a SPEX 800M mixer under an argon atmosphere with hardened steel vials and balls for a fixed time of 5hrs. The ball to power ratio was 20:1 for all samples. Each 30 min of milling was followed by a pause of about 45 min to prevent excessive heating during milling. A Bruker D-8 Advance XRD with Cu K α radiation (λ =0.154060nm) was used to analyze the micro-structural characteristic of the MA samples.

The broadening of XRD was used to calculate the average crystallite size (D). The lattice strain, instrumental effects and crystallite size are the main factors for the broadening of the peaks. The instrumental broadening was corrected using the equation

$\beta = B-b$

Where B is the full width at half maximum (FWHM) calculates by fitting a Lorentzian profile to all the XRD peaks of bcc FeAl alloys using origin software and b is the instrumental broadening. In order to calculate the magnitude of instrumental broadening an XRD pattern of standard silicon powder was used for instrumental calibration. After instrumental calibration, the remaining width β can be considered due to the combine effects of crystallite size and lattice strain.

$$\beta = \beta_s + \beta_c$$

Where β_s and β_c are the FWHM's due to lattice strain and crystallite size respectively.

The Scherrer has derived an expression for broadening of XRD peaks due to crystallite sizes

 $\beta_{crystallite} = \frac{k\lambda}{Dcos\theta}$

Where *k*, λ and θ represent the Scherrer constant, wavelength of the Cu k α radiation used and Bragg diffraction angle. and

β_s= ηtan *θ*

where $\boldsymbol{\eta}$ is the strain in the material.

The lattice parameter (a_0) is calculated using the equation

$$\frac{4\sin^2\theta}{\lambda^2} = \frac{h^2 + k^2 + l^2}{a_0^2}$$

The interplanar planar spacing 'd' was obtained using bragg's law

 $\lambda=2dsin\theta$

Where h, k, l, θ and λ are miller indices, Bragg diffraction angle and wavelength of Cu K α radiation respectively.

3. Result and Discussion

X-ray diffraction (XRD)

Knowledge of crystal structure is mandatory to understand phenomena like phase transformation, plastic deformation and alloy formation. The size and of the unit cell were calculated using angular positions of the peaks. It is very important to assign the correct miller indices to each peak while indexing the pattern The crystal structure and Bravais lattice of the intermetallic alloys and elemental Fe and Al were determined from the sequence of $h^2 + k^2 + l^2$ values in the XRD pattern (see table. 1-7).

XRD patterns of elemental powders of Al and Fe, unmilledFeAl and Fe_{1-x}Al_x ($0.3 \le x \le 0.6$) are shown in Fig. 1. The elemental powders of Fe and Al and unmilledFeAl were also plotted using origin software so that changes that occur during ball milling could be easily observed and could be compared. XRD pattern of elemental Fe powder has two peaks correspond to bcc Fe (110)& Fe (200) at 44.68° and 65.02°, respectively, whereas elemental Al powder has peaks correspond to fcc Al (111), Al (200)& Al (220) at 38.52°, 44.63° & 65.02° , respectively, which indicates that elemental Fe powder has only Fe phase and elemental Al powder has only Al phase and no other phases were present.In the unmilledFeAl sample, the Fe (110) & Fe (200) peaks superimpose with Al (200) & Al (220) peaks, respectively. All the aforementioned peaks have been determined using JCPDS date.



Figure 1: X-ray diffraction (XRD) patterns of elemental Fe and Al powders, unmilled and 5hrs milled Fe_{1-x}Al_x alloys.

The formation of amorphous phases has not been observed in this study because all the samples were milled for just 5hrs. The XRD patterns illustrate the broadening of the fundamental peaks due to increase in lattice strain and refinement of crystallite during alloying process. During milling, the alloying of the elemental powders takes place due to which the intensity of Al peaks decreases and Fe-Al (110) becomes dominant peak (see fig. 1). After 5hrs of milling, the peaks correspond to Al (111) & Al (311) disappear completely and only the fcc peaks are clearly seen (see fig. 1), suggesting that fcc Al has completely diffused into bcc Fe lattice after milling.V.Sebastian et al. [16] have concluded that the disappearance of Al (111) & Al (311) is due to the replacement of the separate Fe and Al phases of elemental Al & Fe powders by a bcc Fe-Al solid solution during ball milling.

Further all the samples after MA for 5 hours, show crystalline structure and textured mainly along (110) direction, irrespective of the Al content. The high intensity peak at 2θ =44.25° corresponds to Fe₃Al(110) and the other low intensity peaks are due to the reflections from Fe₃Al (100), Fe₃Al (200) and Fe₃Al (211) planes, respectively. It is further interesting to note that along with the Fe₃Al peaks the figure also depicts the presence of a superlattice peaks at 2θ =35.6° Fe₃Al (100) and at 2θ =48.24° Fe₃Al(111). The presence of these new peaks clearly indicates the precipitation and formation of ordered domains of Fe (Al) solid solution in Fe-rich samples, as these peaks are not present in the diffraction pattern of unmilled powder samples. However, the intensity of these superlattice peaks

decreases at higher Al concentration due to increase in disorder as a result of diffusion of Al atoms into Fe lattice.



Figure 2: Crystallite size of $Fe_{1-x}Al_x$ intermetallic alloys samples as a function of x.

During disordering, the lattice expansion occurs, the entropy of the system is dominant and the atoms are located randomly in the bcc lattice of Fe (Al), leading to the formation of an antisite defect in the bcc lattice, thereby, increasing the chances of like atoms being the nearest neighbors, thus an atom occupying the wrong atomic site is possible. Such an arrangement of atoms causes the free energy of Fe (Al) to rise, thus the solid solution becomes thermodynamically metastable and offers very less resistance to grain refinement during the milling process. The indexing details of the XRD Patterns of unmilled Fe, unmilled Al, unmilled FeAl, milled $Fe_{0.7}Al_{0.3}$, milled

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 $Fe_{0.6}Al_{0.4}$, milled $Fe_{0.5}Al_{0.5}$ and milled $Fe_{0.4}Al_{0.6}$ respectively are shown in Table 1-7. These indexing tables of samples were used to calculate lattice parameter (a_o), interplanar spacing (d) and average crystallite size (D).

 Table 2: Results of indexing process on unmilled Fe powder

 complex

sample									
Peak	2θ (°)	$\sin^2\!\theta$	sin²0 sin²0 _{min}	$\frac{\sin^2\theta}{\sin^2\theta_{min}} \times 3$	$h^2 + k^2 + l^2$	hkl			
1	38.5	0.11	1	3	3	111			
2	44.6	0.14	1.33	3.99	4	200			
3	65.0	0.29	2.675	8.025	8	220			
4	78.2	0.40	3.685	11.055	11	311			
5	82.4	0.43	4.024	12.072	12	222			

 Table 1: Results of indexing process on unmilled Al powder

 sample

	sample.										
Peak	2θ (°)	$\sin^2\!\theta$	sin²θ sin²θ _{min}	$\frac{\sin^2\theta}{\sin^2\theta_{min}} \times 2$	$h^2+k^2+l^2$	hkl					
1	44.6	0.14	1	2	2	110					
2	65.0	0.29	2	4	4	200					

Table 3: Result of index	ing the XRD on	unmilledFeAl	powder sample

Peak	2 0 (°)	$\sin^2\!\theta$	sin²θ sin²θ _{min}	$\frac{\sin^2\theta}{\sin^2\theta_{min}} \times 3$	$h^2+k^2+l^2$	Unmixed (hkl) fcc Al	$h^2+k^2+l^2 = even, bcc$ Fe
1	38.47	0.19	1	3	3	111	-
2	44.68	0.14	1.33	3.99	4	200	2 (110)
3	65.08	0.29	2.67	8.01	8	220	4 (200)
4	78.17	0.40	3.68	11.04	11	311	-
5	82.31	0.43	4.00	12	12	222	6 (211)

Table 4: Result of indexing the XRD on unmilled Fe_{0.7}Al_{0.3} powder sample

Peak	2 ∂ (°)	sin ² 0	sin²θ sin²θ _{min}	$\frac{\sin^2\theta}{\sin^2\theta_{min}} \times 4$	$h^2+k^2+l^2$	Unmixed (hkl) fcc Al	$h^2+k^2+l^2 = even, bcc$ Fe
1	44.29	22.1	1	4	4	200	2 (110)
2	48.53	24.3	1.19	4.76	5	-	-
3	64.58	32.3	2.010	8.04	8	220	4 (200)
4	73.46	36.7	2.521	10.084	10	310	5 (210)
5	81.51	40.7	3	12	12	222	6 (211)

Table 5: Result of indexing the XRD on unmilled Fe_{0.6}Al_{0.4} powder sample

Peak	2 ∂ (°)	$\sin^2\!\theta$	sin²θ sin²θ _{min}	$\frac{\sin^2\theta}{\sin^2\theta_{min}} \times 4$	$h^2 + k^2 + l^2$	Unmixed (hkl) fcc Al	$h^2+k^2+l^2=even, bcc$ Fe
1	44.10	0.14	1	4	4	200	2 (110)
2	48.19	0.17	1.192	4.768	5	-	-
3	64.04	0.28	2.007	8.028	8	220	4 (200)
4	80.58	0.42	2.985	11.94	12	222	6 (211)

Peak	2 ∂ (°)	$\sin^2\!\theta$	sin²θ sin²θ _{min}	$\frac{\sin^2\theta}{\sin^2\theta_{min}} \times 4$	$h^2 + k^2 + l^2$	Unmixed (hkl) fcc Al	$h^2+k^2+l^2 = even, bcc$ Fe
1	44	0.14	1	4	4	200	2 (111)
2	63.75	0.28	1.99	7.96	8	220	4 (200)
3	80.58	0.42	2.98	11.92	12	222	6 (211)

Table 7: Result of indexing the XRD on unmilled Fe_{0.4}Al_{0.6} powder sample.

Peak	2 0 (°)	$\sin^2\!\theta$	sin²θ sin²θ _{min}	$\frac{\sin^2\theta}{\sin^2\theta_{min}} \times 3$	$h^2 + k^2 + l^2$	Unmixed (hkl) fcc Al	$h^2+k^2+l^2=even, bcc$ Fe
1	38.52	0.11	1	3	3	111	-
2	43.89	0.14	1.2844	3.852	4	200	2 (110)
3	65.02	0.29	2.656	7.968	8	220	4 (200)
4	80.28	0.41	3.819	11.457	12	222	6 (211)

In the end, after milling, Fe-rich phases are formed in case of Fe-rich samples, whereas, Al rich phases dominated as the Al rich content increases. The variation of average crystallite size (D) as a function of $Fe_{1-x}Al_x$ ($0.3 \le x \le 0.6$) is shown in Figure 2. It is observed that with the increase in Al content the average crystallite size reduces exponentially and reduce to about ~6nm after 5hrs of milling.



Figure 3: Integrated intensity of $Fe_{1-x}Al_x$ intermetallic alloys samples as a function of x.

The refinement of crystallite size occurs due to the impactful force of the steel balls on the particles which leads to solid state reaction which is assisted by plastic deformation. The reduction in the integrated intensity of FeAl (110) peak as a function of Fe_{1-x}Al_x, where ($0.3 \le x \le 0.6$), further indicates the formation of FeAl alloy (see figure 3).



Figure 4: Bragg angle of $Fe_{1-x}Al_x$ intermetallic alloys samples as a function of x.



Figure 5: Lattice parameter of $Fe_{1-x}Al_x$ intermetallic alloys samples as a function of x.

The Bragg angles decreases with the increase in Al content (see figure 4), indicating expansion of the bcc lattice and the phase transformation from elemental phases of Fe & Al to bcc Fe(Al) solid solution during ball milling. The value of lattice parameter varies from 0.286nm for unmilledFeAl powder to 0.292 nm for 5hrs milled $Fe_{0.4}Al_{0.6}$ sample due to the formation of disordered Fe(Al),this expanded lattice expansion is shown in Figure 5. The antisite defect is introduced due to lattice expansion during ball milling that means Fe and Al atoms are capable of substituting each other's lattice and antisite defect also increases the possibility of like atoms being the nearest neighbors, hence wrong atomic site could be occupied by an atom. Q.Zeng et al. [9] have also interpreted that changes in peaks intensities, broadening of fundamental peaks and lowering of bragg angle could be due to the diffusion of Al into bcc Fe, refinement of crystallite size and formation of FeAl.

4. Conclusion

In this study, the synthesis and structural analysis of Fe₁₋ $_xAl_x(0.3 \le x \le 0.6)$ samples as a function of x has been reported. The alloying of the samples using ball milling causes the formation of an alloy due to solid state reactions assisted by severe plastic deformation leads to refinement of crystallite size because of which interesting structural properties are evolved during milling. The XRD study confirms the formation of disordered bcc FeAl solid solution after 5hrs of millng, decrease in crystallite size and lattice expansion. It also demonstrates the lowering of bragg angle due to the formation of bccFeAl solid solution. All the samples are mainly textured along the fundamental FeAl (110) peaks and after milling all the samples demonstrate the crystalline structure regardless of the Al concentration. All the aforementioned factors make this FeAl system interesting for further study so that its drawbacks could be eradicated and make it suitable for many applications which are impeded by its drawback these days.

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