

## Evolution of Magnetic Order in Nanocrystalline Fe<sub>1-x</sub>Al<sub>x</sub> Alloy

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(Received 17 July 2022; revised manuscript received 09 August 2022; published online 25 August 2022)

Over the last few decades, ordered intermetallics based on aluminides of transition metals, particularly iron, have been studied for their potential application as high-temperature structural materials. As a result of their superior physical, chemical, and mechanical qualities, such as low density, strong corrosion and oxidation resistance, and high strength at both room and increased temperatures, FeAl intermetallics are becoming increasingly appealing for materials engineering. The magnetic characteristics of Fe<sub>1-x</sub>Al<sub>x</sub> alloys rapidly change with changes in the structural composition and, therefore, are considered as a function of  $x$ . The ball milling operation causes the formation of a solid-state reaction assisted by severe plastic deformation owing to which the crystallite size is lowered, and an unusual and interesting magnetic behavior emerges in the resulting system. <sup>57</sup>Fe Mössbauer spectroscopy is used to investigate the evolution of magnetic order in a high-energy ball-milled Fe-Al solid solution. The Mössbauer spectra of the samples demonstrate the existence of both magnetic and paramagnetic components with the magnetic part including three sub-spectral components. In the Mössbauer spectra of Fe-rich samples, the presence of sextets and the high field component in the hyperfine field distribution (HFD) clearly indicates the high magnetic moment, whereas for the composition  $x = 0.6$ , the presence of sextets indicates the formation of Fe clusters/Fe-rich phases, while the contribution of paramagnetic phases is also clearly visible from HFD for this composition.

**Keywords:** Mechanical alloying, Fe-Al phase, Mössbauer spectroscopy.

DOI: [10.21272/jnep.14\(4\).04020](https://doi.org/10.21272/jnep.14(4).04020)

PACS numbers: 81.20.Ev, 81.07.Bc, 75.75.-c

### 1. INTRODUCTION

Mechanical alloying (MA) is a practical processing route for the synthesis of nanocrystalline mixtures. The MA process leads to the formation of alloys due to solid-state reactions assisted by severe plastic deformation that occurs during ball milling of elemental powders [1, 2]. However, the properties of metals and compounds depend to a large extent on the grain size, the nature and structure of the interfaces formed during processing [3]. In many pure metals and alloys, the reduction of the grain size in the nanometer range is associated with an overall strength increase and a change in the magnetic and electronic behavior [3].

During the last several decades, ordered intermetallics, based on aluminides of transition metals, especially iron, have been under investigation for their possible use as high-temperature structural materials [4-6]. Therefore, FeAl intermetallics are becoming more and more attractive for materials engineering because of their excellent physical, chemical, and mechanical properties, i.e., low density, good corrosion, oxidation resistance, and high strength at both room and elevated temperatures [7-9]. It has been shown that with increasing Al concentration, the oxidation and sulphidization resistances of FeAl alloys increases, while their densities decrease [10]. This makes FeAl intermetallics with high Al concentrations good candidates for structural materials for use in high-temperature hostile environments. However, the widespread use of FeAl intermetallics has been limited by their inherently low ductility and toughness, especially at ambient temperatures. Higher percentages of Al in FeAl intermetallics reduce the ductility [11, 12]. However, it is reported that strong enhancement of diffusivity in

nanophase materials [13], attributed to grain-boundary mechanisms, should have relevant consequences on the ductility at relatively low temperatures. Therefore, two main approaches were generally followed to improve the ductility. The first approach includes careful control of grain-boundary cohesion by micro-alloying and the second includes the improvement of the suitable grain refinement processing, such as inoculation, rapid solidification, and MA techniques [14]. The MA technique is receiving particular attention, as it is suitable for the production of nanophase materials on an industrial scale.

The magnetic behavior of Fe-rich FeAl alloys also readily changes with changes in their structural composition. This change is very prominent and easily observable for even very small mechanical deformation on ordered alloy [15, 16] providing great ease to undergo order-disorder transitions. It is recorded that a solid solution structure is induced with simple milling and the lattice parameter increases by 1 % in some compositions of alloys and within no time variation, magnetic behavior exhibits this change e.g., a few ordered samples show a paramagnetic nature, but on being milled they become ferromagnetic. These behaviors are explained on the basis of the close relationship between the microstructure and magnetism. The studies of  $3d$  based magnetic materials like FeAl system provide fundamental clarity for a basic understanding of magnetism. These magnetic materials find many applications in the industrial world, which is why any study that can help to understand the origin of the magnetic properties of this kind of materials could be used to improve them or to produce materials adapted or optimized for each application. These two reasons make the study of magnetic interactions between  $3d$  magnetic

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elements, magnetic effects, and the properties present in the magnetic materials formed very important in the world of magnetism research. It is suitable to study quantitatively the role of the structure on magnetism in FeAl alloys as they have well-known ordered structures for studying the basic properties.

The electronic properties of FeAl-based alloys are also interesting, as there are changes in the structure, magnetic coupling, binding energy, *s-p* hybridization, etc. during the alloying process. Generally, there is scant literature describing the transport properties of the FeAl system, and in the past, several authors have performed band structure calculations in an attempt to understand the electronic structure of FeAl systems. B.V. Reddy et al. have calculated the electronic structure of iron-aluminides ( $\text{Fe}_{1-x}\text{Al}_x$ ) for a range of Al concentrations ( $0 \leq x \leq 0.5$ ) [17]. The present experimental and previous theoretical studies suggest that the change in the electronic properties can be attributed to the continuous change in the electronic structure due to the strong hybridization of Fe and Al near the Fermi level as a result of charge transfer.

In the present work, we discussed in detail the magnetic properties of  $\text{Fe}_{1-x}\text{Al}_x$  alloys prepared by MA. The magnetic hyperfine field distributions (HFD) obtained from the  $^{57}\text{Fe}$  Mössbauer spectra were used to identify different magnetic phases in terms of the nearest neighbors of Al to Fe. The dependence of the bulk magnetic properties on the microstructure and hyperfine magnetic fields was discussed qualitatively.

## 2. EXPERIMENTAL DETAILS

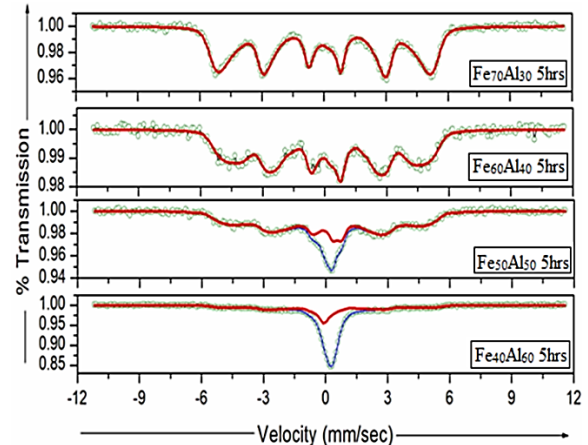
Intermetallic  $\text{Fe}_{1-x}\text{Al}_x$  alloy powders were prepared by high energy MA of analytical grade Fe and Al powders with purities of 99.9 % and size less than 100  $\mu\text{m}$ . The powders were initially mixed thoroughly using an agate pestle and mortar and then sealed in a cylindrical vial under an argon atmosphere with tungsten carbide balls to prevent oxidation phenomena. Then each powder sample was dry-milled in a SPEX 8000M high-energy mixer-mill for a fixed time of 5 h. The speed of the SPEX mixer mill was 1080 rpm. Six balls with a diameter of 0.25 and a combined mass of 22 g were used at a ball-to-powder ratio of 20:1 for all studies. To avoid excessive heating during milling, each 30 min of milling was followed by a pause of 1 h in Ar atmosphere.

The microstructure of the nanocrystalline powder was characterized using  $^{57}\text{Fe}$  Mössbauer spectroscopy in the transmission mode to study local magnetic and non-magnetic phases. Mössbauer spectroscopy measurements were carried out using a conventional constant-acceleration PC-based spectrometer equipped with a WissEl velocity drive,  $^{57}\text{Co}$  (Rh) source, and calibrated with a metallic iron foil at room temperature.

## 3. RESULTS AND DISCUSSION

A conventional constant-acceleration PC-based spectrometer was used to carry out transmission  $^{57}\text{Fe}$  Mössbauer measurements. The spectrometer was equipped with WissEl velocity drive,  $^{57}\text{Co}$  (Rh) source, and calibrated with a metallic iron foil at room temperature. The room temperature Mössbauer spectra of the

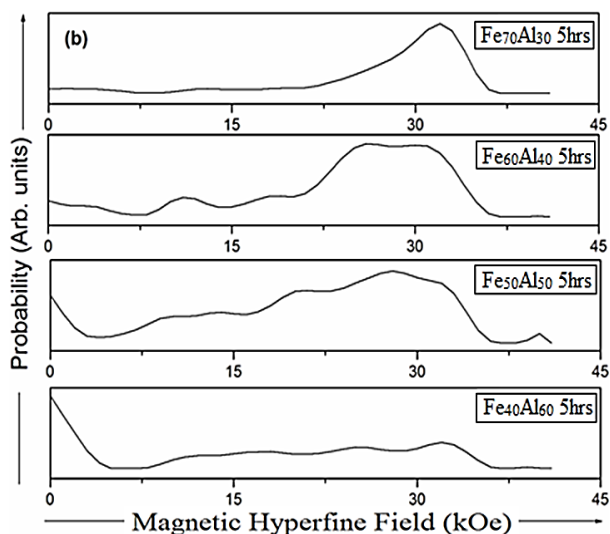
5 h milled  $\text{Fe}_{1-x}\text{Al}_x$  samples are shown in Fig. 1 and the corresponding HFD are shown in Fig. 2. The parameters related to the Mössbauer spectra are shown in Table 1. The spectra of the milled samples consist mainly of a broad sextet characteristic of disordered alloys and quadrupole doublet. On fitting for discrete Lorentzians, the width of the magnetic sextet is seen to be large compared to the width of the Fe inner peak (0.24 mm/s), indicating HFD since the  $^{57}\text{Fe}$  Mössbauer spectra of disordered systems consist of a number of close-lying, unresolved subspectra. The spectra have therefore been refitted using Windows [18] program for HFD (Fig. 2). The distribution program gives the magnetic hyperfine fields at  $^{57}\text{Fe}$  sites in different environments in terms of the probability of occurrence  $P(H)$  as a function of the magnetic hyperfine field  $H$ . The negative values of  $P(H)$  have no physical meaning and are mostly because of the statistical fluctuations in the background [19]. While fitting this method, the ratio between the intensities of the first and third peaks of the sextets has been constrained to be three, and the ratio between the intensities of the second and third peaks has been used as a free parameter. The data of  $\text{Fe}_{40}\text{Al}_{60}$  and  $\text{Fe}_{50}\text{Al}_{50}$  are fitted with HFD and one central doublet, whereas the data of  $\text{Fe}_{60}\text{Al}_{40}$  and  $\text{Fe}_{70}\text{Al}_{30}$  are fitted with only HFD.



**Fig. 1** – Room-temperature Mössbauer spectra of  $\text{Fe}_{1-x}\text{Al}_x$  ( $x = 0.3, 0.4, 0.5, 0.6$ ) samples milled for a fixed time of 5 h. The dots are experimental data and lines represent the fit

The Mössbauer spectra and HFD of the samples show the presence of both magnetic and paramagnetic components with the magnetic part containing three sub-spectral components. In the Mössbauer spectra of Fe-rich samples, the presence of sextets and the high field component in HFD clearly indicates the high magnetic moment, whereas for the composition  $x = 0.6$  the presence of sextets indicates the formation of Fe clusters/Fe-rich phases. In the case of the composition  $x = 0.6$ , the contribution of paramagnetic phases is also clearly visible from HFD (Fig. 2), and as iron-rich phases start to form, the paramagnetic contribution decreases with a corresponding increase in the hyperfine field. For Al-rich samples, it is expected that the final alloy should also be Al-rich. Hence the presence of a quadrupole doublet due to the formation of a nonmagnetic Al-rich FeAl alloy and a low field HFD component, which can be

attributed to the presence of Al-rich grains [20], is as expected. Since Al-rich phases are paramagnetic, the presence of Fe-rich phases is important from a magnetic point of view, as they should be responsible for the bulk magnetic properties of this system.



**Fig. 2** – HFD of the Mössbauer spectra for 5 h milled  $\text{Fe}_{1-x}\text{Al}_x$  ( $x = 0.3, 0.4, 0.5, 0.6$ ) samples

Since the ball milling method used in the present study is a high-energy process, and also the ball-to-powder ratio used is large, the probability of formation of isolated Fe in a cubic environment, which would give rise to a singlet, is small. Analysis of the Mössbauer spectra shows that the area under the quadrupole doublet is maximum for  $x = 0.6$ . The initial composition of this sample is the same as that of the  $\text{FeAl}_2$  composition. The value for quadrupole splitting is  $0.22 \pm 0.03$  mm/s and the value of isomer shift is  $0.29 \pm 0.01$  mm/s. Hence, this composition has the ma-

ximum paramagnetic phase. Therefore, it is possible that the formation of stoichiometric  $\text{FeAl}_2$  alloy, which is paramagnetic, is favored in this sample. Since this composition has the maximum paramagnetic phase, it is expected that the values of bulk magnetic parameters such as saturation magnetization ( $M_s$ ) and area under the loop would be minimum for the sample with  $x = 0.6$ . To confirm the same bulk magnetization study is required using a vibrating sample magnetometer.

**Table 1** – Mössbauer parameters: isomer shift (IS), quadrupole splitting (QS), average magnetic hyperfine field (BHF), percentage area occupied by quadrupole peaks in the Mössbauer spectrum, and FWHM of quadrupole peaks for  $\text{Fe}_{1-x}\text{Al}_x$  ( $x = 0.3, 0.4, 0.5, 0.6$ ) powder samples ball milled for a fixed period of 5 h

Sample	IS (mm/s)	QS (mm/s)	BHF (Tesla)	Area (%)	FWHM (mm/s)
$\text{Fe}_{40}\text{Al}_{60}$	$0.29 \pm 0.01$	$0.22 \pm 0.03$	16.9	47 53	0.41 $0.62 \pm 0.02$
$\text{Fe}_{50}\text{Al}_{50}$	$0.14 \pm 0.06$	$0.30 \pm 0.06$	21.44	84.4 15.6	0.41 $0.59 \pm 0.11$
$\text{Fe}_{60}\text{Al}_{40}$	–	–	24.02	100	0.41
$\text{Fe}_{70}\text{Al}_{30}$	–	–	27.56	100	0.41

#### 4. CONCLUSIONS

The study of  $\text{Fe}_{1-x}\text{Al}_x$  intermetallic alloy as a function of Al content prepared by ball milling has given fascinating results. The ball milling process leads to the formation of a solid-state reaction assisted by severe plastic deformation, due to which the crystallite size decreases, and interesting magnetic properties develop in the resulting system. For Fe-rich samples, the high magnetic moment is confirmed by the sextets and the high field component in the HFD. On the other hand, for the composition  $x = 0.6$ , HFD shows the presence of both magnetic (Fe-rich) and paramagnetic phases.

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**Еволюція магнітного порядку в нанокристалічному сплаві  $\text{Fe}_{1-x}\text{Al}_x$** 

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Протягом останніх кількох десятиліть впорядковані інтерметаліди на основі алюмінідів перехідних металів, зокрема заліза, вивчалися на предмет їх потенційного застосування як високотемпературних конструкційних матеріалів. Завдяки своїм чудовим фізичним, хімічним і механічним властивостям, таким як низька густина, висока стійкість до корозії та окислення, а також висока міцність як при кімнатній, так і при підвищених температурах, інтерметаліди FeAl стають все більш привабливими для матеріалознавства. Магнітні характеристики сплавів  $\text{Fe}_{1-x}\text{Al}_x$  швидко змінюються зі зміною структурного складу і тому розглядаються як функція  $x$ . Техніка подрібнення в кульовому млині викликає утворення твердотільної реакції, якій сприяє сильна пластична деформація, завдяки чому розмір кристалітів зменшується, і в отриманій системі виникає незвичайна та цікава магнітна поведінка. Мессбауерівська спектроскопія  $^{57}\text{Fe}$  використовується для дослідження еволюції магнітного порядку у високоенергетичному твердому розчині Fe-Al, подрібненому в кульовому млині. Мессбауерівські спектри зразків демонструють існування як магнітних, так і парамагнітних компонентів, причому магнітна частина включає три субспектральні компоненти. У Мессбауерівських спектрах зразків, збагачених залізом, наявність секстетів і компоненти сильного поля у надтонкому розподілі поля (HFD) чітко вказує на високий магнітний момент, тоді як для складу  $x = 0.6$ , наявність секстетів вказує на утворення кластерів заліза/багатих залізом фаз, у той час як внесок парамагнітних фаз також чітко видно з HFD для цього складу.

**Ключові слова:** Механічне легування, Фаза Fe-Al, Мессбауерівська спектроскопія.