

## TEM and XPS Study of Ball-Milled Fe<sub>1-x</sub>Al<sub>x</sub> Alloys

Ranjeet Brajpuria<sup>1,\*</sup>, Rajeev Gupta<sup>1</sup>, Ankush Vij<sup>1</sup>, Ashish Kumar<sup>1</sup>, Snehal Jani<sup>2</sup>

<sup>1</sup> Applied Science Cluster, University of Petroleum & Energy Studies, 248001 Dehradun, Uttarakhand, India

<sup>2</sup> Department of Physics, Amity University Madhya Pradesh, Gwalior, India

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The ball milling technique has been extensively used to prepare different metastable states with nanocrystalline microstructures from intermetallic compounds. In the present manuscript, the authors have systematically investigated the structural and electronic properties of a series of mechanically alloyed Fe<sub>1-x</sub>Al<sub>x</sub> (0.3 ≤ x ≤ 0.6) samples using transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The ball milling process causes the formation of solid-state reactions that are aided by severe plastic deformation, resulting in reduced crystallite size and interesting microstructural and electronic changes in the resulting system. The TEM results show that the crystallite size decreases to the nanometer range (between 6-8 nm) as a function of x and the metals dissolve at the nanograin boundaries. As a result of nanometric dimensions, the reactivity increases as a result of the increased surface-to-volume ratio, which leads to the FeAl alloy phase formation. The XPS survey scan shows that the samples do not have any major contamination, and the core level spectra show a slight shift of Fe<sub>2p</sub> and Al<sub>2p</sub> peaks toward higher binding energy (BE), which proves that different Fe- and Al-rich phases of FeAl alloy have formed after 5 h of milling.

**Keywords:** XRD, Thin film, Nanocrystalline, Interface, Amorphous.

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### 1. INTRODUCTION

Intermetallic compounds have caught the attention of scientists for decades due to their exceptional characteristics. Ordered intermetallics based on transition metal aluminides, particularly with iron, have been studied for their potential application as high-temperature structural materials [1-5]. As a result of their superior physical, chemical, and mechanical characteristics, FeAl intermetallics are becoming increasingly appealing to materials scientists. It has been shown that an increase in the Al content enhances the oxidation and sulfidation resistance of FeAl alloys while lowering their density [6-9]. This makes FeAl intermetallics with high Al concentrations suitable for structural materials used in harsh environments. But these intermetallics have not been widely used because they are not very flexible at room temperature [10-13]. Making fine-grained materials, on the other hand, has been suggested as a possible way to improve room temperature ductility [14, 15].

The mechanical alloying (MA) process leads to a refinement of the grains accompanied by the evolution of the system through different metastable phases due to which there is a notable change in the microstructural and mechanical properties. SEM and TEM studies also show that structural changes take place during alloy formation and these changes are very much interesting due to their direct application in the industrial sector. The electronic properties of FeAl-based alloys are also of interest, as there are changes in the structure, magnetic coupling, binding energy, s-p hybridization, etc. during the alloying process [16]. In the present work, the authors have discussed in detail the microstructural and electronic properties of Fe<sub>1-x</sub>Al<sub>x</sub> alloys prepared by MA. The variation in particle size and phase for-

mation has been determined using TEM whereas the change in chemical and electronic structure has been studied with X-ray photoelectron spectroscopy (XPS).

### 2. EXPERIMENTAL DETAILS

Fe<sub>1-x</sub>Al<sub>x</sub> (x = 0.3, 0.4, 0.5, and 0.6) alloys were prepared by high-energy MA of analytical grade Fe and Al powders of approximately 100 μm size and with purities of 99.9%. From here onwards, Fe<sub>0.7</sub>Al<sub>0.3</sub>, Fe<sub>0.6</sub>Al<sub>0.4</sub>, Fe<sub>0.5</sub>Al<sub>0.5</sub> and Fe<sub>0.4</sub>Al<sub>0.6</sub> samples are referred to as Fe<sub>7</sub>Al<sub>3</sub>, Fe<sub>6</sub>Al<sub>4</sub>, Fe<sub>5</sub>Al<sub>5</sub>, and Fe<sub>4</sub>Al<sub>6</sub>. The powders were initially mixed thoroughly using an agate pestle and mortar and then dry-milled in an argon atmosphere using a SPEX 8000M high-energy mixer/mill with hardened steel vials and balls for a fixed time of 5 h. To avoid excessive heating during milling, each 30 min of milling was followed by a pause of 1 h under Ar atmosphere. Microstructural characterization of the milled powders was performed by using TEM.

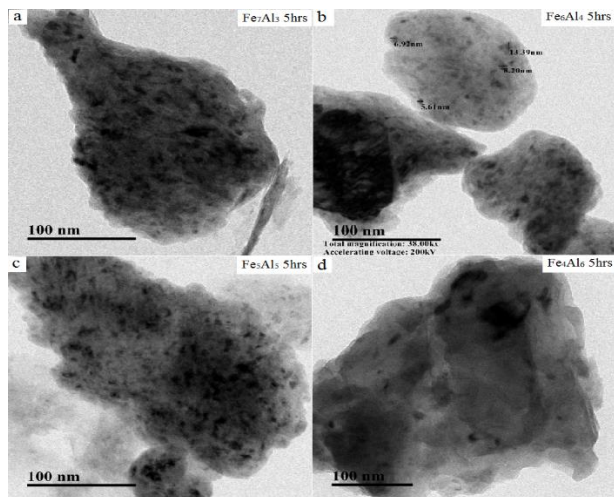
The XPS technique is used to identify the possibilities of in-equivalence in the samples prepared. Chemical and electrical information about the samples is obtained using XPS at various depths utilizing Mg-Kα radiation at a base pressure greater than 5 × 10<sup>-9</sup> Torr. Mg-Kα radiation was emitted from a source operated at an emission current of 10 mA and an anode voltage of 10 kV. A concentric hemispherical energy analyzer (CHA) with a pass energy of 50 eV was utilized, yielding an overall resolution of 0.9 eV. To correct shifts of the binding energy (BE) of core levels caused by the charging effect, an external reference of Au 4f<sub>7/2</sub> at 84.7 eV and an internal reference graphitic C-1s peak at 284.7 eV were used. All measurements were taken at constant room temperature.

\* [ranjeetbjp1@gmail.com](mailto:ranjeetbjp1@gmail.com)

### 3. RESULTS AND DISCUSSION

#### 3.1 Transmission Electron Microscopy (TEM) Measurements

Fig. 1 shows the TEM images of a series of 5 h ball-milled  $\text{Fe}_{1-x}\text{Al}_x$  ( $x = 0.3, 0.4, 0.5, 0.6$ ) alloy powder samples. The color contrast in the TEM micrograph of the unmilled sample is mainly due to the difference in atomic number ( $Z$ ). Since Fe ( $Z = 26$ ) has a much larger electron scattering form factor than Al ( $Z = 13$ ), in the bright-field image there will be less contribution from Fe regions than from Al regions, and hence the Fe crystallites appear darker as compared to Al.



**Fig. 1** – TEM micrographs of  $\text{Fe}_{1-x}\text{Al}_x$  ( $x = 0.3, 0.4, 0.5$  and  $0.6$ ) samples at room temperature

The average crystallite sizes measured from TEM are shown in Fig. 1. The diameter of a nanoparticle is found by taking the average of its diameters as seen in TEM images from different directions. It shows that the average crystallite size decreases drastically in all the cases as compared to the unmilled sample. However, the average crystallite size is found to be in the range of 6 to 8 nm, irrespective of the sample concentration. This may be a result of the progressive accumulation and interaction of dislocations, leading to the continuous refinement of crystallite size, yielding nanometric structures as well as an increase in lattice strain. When this structure is milled on for a long time, it changes into a fully nanocrystalline structure where the orientation of neighboring crystallites is completely random, and they are separated by high-angle grain boundaries.

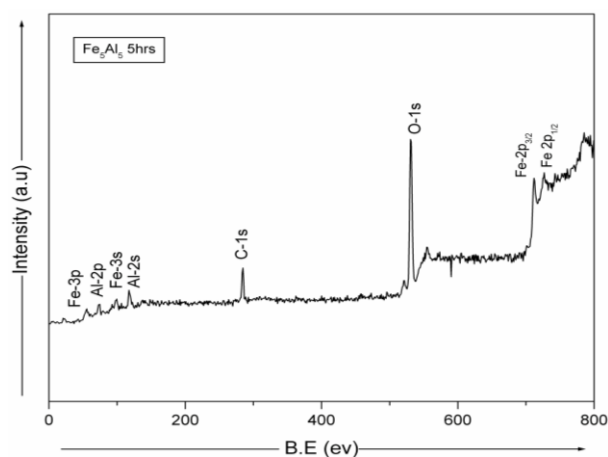
#### 3.2 X-ray Photoelectron Spectroscopy (XPS) Measurements

As already discussed, XPS is the most powerful and quantitative technique for elemental characterization. Therefore,  $\text{Fe}_{1-x}\text{Al}_x$  alloy samples milled for 5 h were used for the XPS study to get information about changes in the BE position as a result of phase formation.

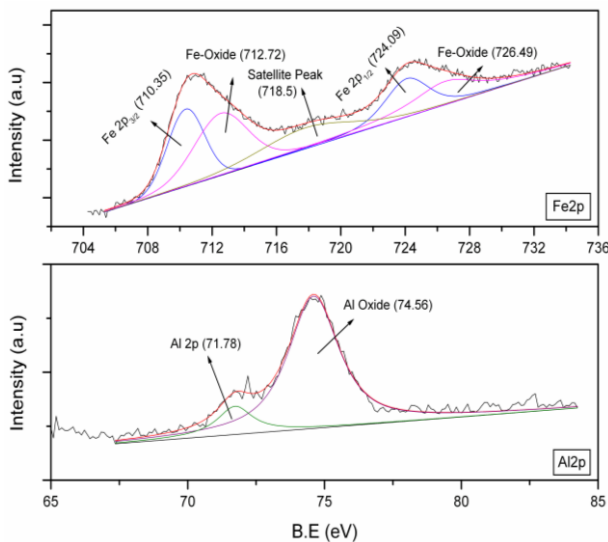
The survey scan of the  $\text{Fe}_5\text{Al}_5$  unmilled powder sample is shown in Fig. 2. The unmilled sample clearly shows two prominent peaks of Carbon ( $\text{C}_{1s}$ ) at 284.7 eV and Oxygen ( $\text{O}_{1s}$ ) at 532.4 eV as compared to other

small peaks of Iron (Fe) and Aluminum (Al). The prominent signals of Oxygen and Carbon might be due to the atmospheric exposure during the sample transfer in the XPS chamber. To gain more insight into the elements, separate detailed scans have been recorded for Iron and Aluminum.

The core level spectra of  $\text{Fe}_{2p}$  and  $\text{Al}_{2p}$  of the unmilled  $\text{Fe}_5\text{Al}_5$  powder sample are shown in Fig. 3. Using the standard XPS peak fit 4.1 software, the detailed scan spectra of  $\text{Fe}_{2p}$  and  $\text{Al}_{2p}$  were de-convoluted. The data were normalized to the  $\text{C}_{1s}$  peak position at a BE position of  $\sim 284.6$  eV. The recorded spectrum of Fe shows some significant differences, which are characteristics of the oxidized state.



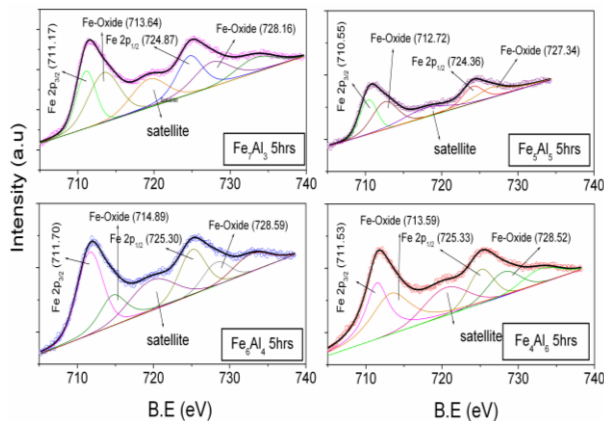
**Fig. 2** – Survey scan of the  $\text{Fe}_5\text{Al}_5$  alloy sample milled for 5 h



**Fig. 3** – Core-level spectra of  $\text{Fe}_{2p}$  and  $\text{Al}_{2p}$  for an unmilled sample of  $\text{Fe}_5\text{Al}_5$

In order to analyze the results more precisely, the  $\text{Fe}_{2p}$  peak was de-convoluted into two peaks, one of which corresponds to the metallic phase of Fe and the other to the oxide state of Fe. A satellite peak is also observed at a BE position of  $\sim 718.5$  eV, which is  $\sim 8.05$  eV higher than the  $\text{Fe}_{2p_{3/2}}$  peak. Furthermore, the  $2p$  spin-orbit effect divides the  $\text{Fe}_{2p}$  spectrum into the  $2p_{3/2}$  and  $2p_{1/2}$  parts, and the continuous tail is caused by electron-hole pair excitations and is a char-

acteristic of metallic states. In the same way, the  $\text{Al}_{2p}$  core level is also fitted with two peaks, one of which corresponds to metallic Al and the other to the oxide state of Al. It is worth noting that the relative intensity of the  $\text{Al-O}_x$  peak is greater than that of the elemental  $\text{Al}_{2p}$  peak. This suggests that oxygen interacted to a greater extent with Al and partially with Fe (Fig. 3).



**Fig. 4** – Core-level spectra of  $\text{Fe}_{2p}$  of the  $\text{Fe}_{1-x}\text{Al}_x$  alloy samples milled for 5 h

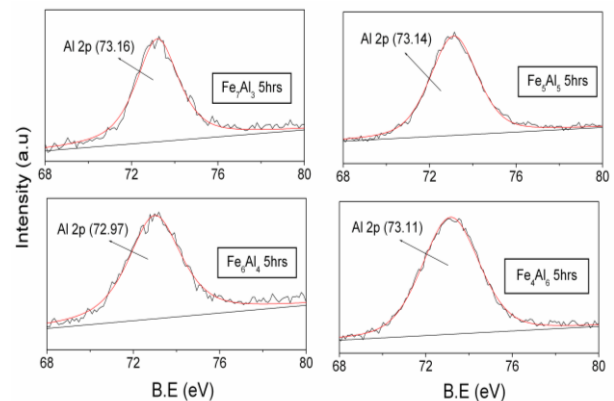
Drastic changes are visible in the core level spectra of both  $\text{Fe}_{2p}$  and  $\text{Al}_{2p}$  after 5 h of milling (see Fig. 4 and Fig. 5, respectively). It is attention-grabbing to find out that when the sample is milled for 5 h, the  $\text{Fe}_{2p_{3/2}}$  core level peak is followed by 711.17 eV for  $\text{Fe}_7\text{Al}_3$ , 711.70 eV for  $\text{Fe}_6\text{Al}_4$ , 710.55 eV for  $\text{Fe}_5\text{Al}_5$ , 711.53 eV for  $\text{Fe}_4\text{Al}_6$ . A meticulous study of the data shows that the peak position is shifted by 0.1 to 1.25 eV towards higher BE compared to the  $\text{Fe}_{2p_{3/2}}$  core line of the unmilled sample. Analogous changes are observed in the  $\text{Al}_{2p}$  core level as indicated in Fig. 5. Standardized to the  $\text{Al}_{2p}$  core line, the  $\text{Al}_{2p}$  core line is also shifted by  $\sim 1.4$  eV towards a higher BE as compared to the unmilled sample. These changes in  $\text{Fe}_{2p}$  and  $\text{Al}_{2p}$  core lines are clearly seen in the alloy formation in the samples.

If we compare the samples of the  $\text{Fe}_{1-x}\text{Al}_x$  ( $x = 0.3, 0.4, 0.5, \text{ and } 0.6$ ) system, we find some differences in the BE positions of  $\text{Fe}_{2p}$  and  $\text{Al}_{2p}$  core lines. The BE of the  $\text{Fe}_{2p}$  and  $\text{Al}_{2p}$  peaks is shifted towards a higher BE compared to their elemental peak position. Additionally, depending on the atomic percentage of the Al content in

the FeAl alloy, the shift of the peak position is different in different cases. The different shift in each case is due to the formation of various phases of Fe- and Al-rich FeAl alloy.

#### 4. CONCLUSIONS

The study of the  $\text{Fe}_{1-x}\text{Al}_x$  ( $x = 0.3, 0.4, 0.5, 0.6$ ) intermetallic alloy as a function of  $x$  prepared by ball milling has given interesting results. The ball milling process causes the formation of solid-state reactions that are aided by severe plastic deformation, resulting in reduced crystallite size and interesting microstructural and electronic changes in the resulting system. The TEM study shows major structural changes (nanocrystallization and FeAl alloy formation) after 5 h of milling. Additionally, amorphization also increases as a result of milling with an increase in  $x$ . The survey scan during XPS measurements shows that contamination is on the surface only, and  $\text{Fe}_{2p}$  and  $\text{Al}_{2p}$  peaks are shifted towards higher binding energy, which can be attributed to the formation of various Fe- and Al-rich phases of the FeAl alloy.



**Fig. 5** – Core-level spectra of  $\text{Al}_{2p}$  of the  $\text{Fe}_{1-x}\text{Al}_x$  alloy samples milled for 5 h

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**Дослідження сплавів  $Fe_{1-x}Al_x$ , подрібнених у кульовому млині,  
за допомогою TEM та XPS**Ranjeet Brajpuriya<sup>1</sup>, Rajeev Gupta<sup>1</sup>, Ankush Vij<sup>1</sup>, Ashish Kumar<sup>1</sup>, and Snehal Jani<sup>2</sup><sup>1</sup> *Applied Science Cluster, University of Petroleum & Energy Studies, 248001 Dehradun, Uttarakhand, India*<sup>2</sup> *Department of Physics, Amity University Madhya Pradesh, Gwalior, India*

Техніка подрібнення в кульовому млині широко використовується для отримання різних метастабільних станів з нанокристалічними мікроструктурами з інтерметалічних сполук. У статті автори систематично досліджували структурні та електронні властивості серії механічно легованих зразків  $Fe_{1-x}Al_x$  ( $0.3 \leq x \leq 0.6$ ) за допомогою просвічуючої електронної мікроскопії (ТЕМ) та рентгенівської фотоелектронної спектроскопії (ХРС). Процес подрібнення в кульовому млині викликає протікання твердотільних реакцій, яким сприяє сильна пластична деформація, що призводить до зменшення розміру кристалітів і цікавих мікроструктурних та електронних змін у отриманій системі. Результати ТЕМ показують, що розмір кристалітів зменшується до нанометрового діапазону (між 6-8 нм) як функція  $x$ , і метали розчиняються на межах нанозерен. Через нанометричні розміри реакційна здатність підвищується в результаті збільшення співвідношення поверхні до об'єму, що призводить до утворення фази сплаву FeAl. Оглядове сканування ХРС показує, що зразки не мають серйозного забруднення, а спектри рівня ядра демонструють невеликий зсув піків  $Fe_{2p}$  та  $Al_{2p}$  у бік вищої енергії зв'язку (ВЕ), що доводить, що різні багаті на Fe та Al фази сплаву FeAl утворилися після 5 годин подрібнення.

**Ключові слова:** XRD, Тонка плівка, Нанокристалічний, Межа розділу, Аморфний.