Chapter 6
CHAPTER - 6

EFFECT OF Ga SUBSTITUTION ON THE PHASE STABILITY OF Fe-Mn-Al(Ga) HEUSLER ALLOYS

6.1 INTRODUCTION

Because of its interesting and unique properties and easy tunability Fe containing Heusler alloys has been widely studied. All such Fe containing Heusler alloys compounds follows the Slater-Pauling behavior (Galanakis, 2016). To follow the Slater-Pauling curve the Fe in Fe$_2$MnAl has small negative magnetic moment while in Fe$_2$CrAl it behaviors practically nonmagnetic. Experimentally it has been found that Fe$_2$VAI is a semi-metal and having total 24 valence electrons (Feng et al., 2001; Lue et al., 2001; Nishino et al., 2001; Matsushita et al., 2002). For the Fe$_2$MnAl and Fe$_2$CrAl alloys the Mn and Cr atoms have comparable spin moments to that of Co compounds and have similar density of state. When in Fe$_2$MnAl Heusler compound Al is replaced by Si, the Fe spin-up state is exclusively populated by the extra electron the spin moment of each Fe atom is increased by 0.5 $\mu$B and also the spin moment of the Mn atoms increases remarkably (Heusler, 1903). A drastic change in the optical and electrical properties in the Fe$_2$MeAl alloys (Me = Ti, V, Cr) has been reported by Shreder et al. (2008). Liu et al. (2011) investigated the connection between magnetic structure and electrical resistance anomaly and observed metal-semiconductor transition at 150K and semiconductor-metal transition at 51K for Fe$_2$MnAl Heusler alloy ribbons. In order to investigate the structural, magnetic and electronic properties of Fe$_{3-x}$Mn$_x$Z (Z= Al, Ge, Sb), full-potential linearized augmented plane-wave (FP-LAPW) method was employed and it has been observed that to tune the physical properties the change in the main group element is a strong tool (Azar et al., 2012). In this case Mn rich compounds shows the high spin polarization while increasing the Fe content compounds become metallic with low spin polarization.

The magnetic and electronic properties of the Fe-based Heusler alloys have been studied under the experimental and theoretical methods (Paduani et al., 2007; Dahmane et al., 2016; Umetsu et al., 2012). C. Paduani et al. (2007) have reported that for the Fe-based full Heusler with L2$_1$ structure, at low temperature the spin glass
behavior was noticed and strong compositional dependency of Curie temperature. F. Dahmane et al. (2014) studied magnetic, structural, and electronic properties of Fe$_2$XAl (X = Cr, Mn, Ni) systems and reported that the Fe$_2$NiAl have a metallic and Fe$_2$XAl (X = Cr, Mn) are half metallic in nature with total magnetic moments of 2 $\mu$B and 1 $\mu$B, respectively. Jain et al. (Rakesh et al., 2014a; Vivek et al., 2014; Vishal et al., 2014; Rakesh et al., 2014b) have studied the structural and magnetic properties of many Fe- and Co-based Heusler alloys such as Fe$_2$MnAl and Co$_2$MnAl. They reported that these alloys (Fe$_2$MnAl and Co$_2$MnAl) possess high Curie temperature and high magnetic moment and stabilize in L2$_1$ or ordered B2 structures. The exchange bias behavior has been observed in high-energy ball-milled Fe$_2$MnAl alloys (Vinesh et al., 2009; Vinesh et al., 2014; Jain et al., 2014). Paduani et al. have observed the structural stability of ordered L21 structure for Fe$_2$MnAl alloys and noticed that it remains stable with small deviations from the stoichiometric 2:1:1 of composition (Paduani et al., 2007; Paduani et al., 2008). Although the largest moment is carried by Mn atoms in the ordered phase of Fe$_2$MnAl alloys yet decreases with the increase in Mn concentration the saturation magnetic moment and hence the saturation magnetization was found be strongly composition dependent (Paduani et al., 2007; Paduani et al., 2008). Generally, in quaternary Heusler alloys one out of four sites is occupied by two unlike elements. Such ease in the chemical variability make feasible to produce several mixed (quaternary) Heusler alloys. It is easy to obtain the many ordered compounds by simple heat treatment (Galanakis et al., 2004; Go, 2015). For Fe$_2$YZ Heusler alloys compounds the Curie temperature and Half metallicity was mainly depend upon the element at that Y site. For instance, the Mn has greater magnetic moment than the Ti, Ni etc. and hence by selecting the suitable element at the Y and Z sites one can obtain the desired structural, optical and magnetic properties in Fe$_2$MnAl Heusler alloy (Shreder et al., 2012; Yin et al., 2015; Belkhouane et al., 2015; Kourov et al., 2015; Azar et al., 2012).

temperature to 873 K and decreases sharply above this temperature. On the experimental analysis of Fe-Ti-Al alloys it has been noticed that the hardness and strength increases remarkably if the two or more phases (α-Fe, Fe2Ti (Laves phase) and/or Fe2TiAl) was present in the alloy (Prakash and Sauthoff 2001). The thermal conductivity of Fe-Ti-Al alloy was found to be fairly low 20 WmK⁻¹ (Nakata et al. 1996). Wittmann et al. (2001) have investigated L2₁–structured (Fe,Ni)2MnAl based alloys reported that for similar composition, single phase alloy exhibits the value of hardness 310VPN while greater hardness (445-539 VPN) was observed for alloys having multi-phase spinodal microstructure. The structural defects and mechanical properties of off-stoichiometric Fe₂MnAl single crystal have been studied and found that with increase in the quench temperature (up to 1100 K) the yield strength increases (Wittmann et al. 2004).

In the present work, we have reported the results of the observations of the structural and mechanical properties of the Ga-substituted Fe₅₀Mn₂₅Al₂₅₋ₓGaₓ alloys (x = 0, 2.5, 5.0, 7.5, 10.0) to get a series with general formula Fe₅₀Mn₂₅Al₂₅₋ₓGaₓ 0 ≤ x ≤ 10, we have chosen the Ga as a doping element at the Al site starting with the parent stoichiometric composition Fe₅₀Mn₂₅Al₂₅.

6.2. EXPERIMENTAL DETAILS

6.2.1 Synthesis

The polycrystalline ingot of Fe₅₀Mn₂₅Al₂₅₋ₓGaₓ alloy with nominal composition x= 0, 2.5, 5.0, 10.0 has been prepared by means of induction melting, in dynamic argon atmosphere. The purity of the constituent elements (Fe, Mn, Al, Ga) was ~99.99%. The constituents were palletized by hydraulic pressure into a circular button of the diameter of 15mm. this button was placed into quartz tube surrounded by another Pyrex glass jacket with cold water flow through the outer jacket. To create the inert atmosphere a continuous flow of the argon was made. The ingots were re-melted four times to get the samples homogenized. For sake of simplicity the short form of the samples (Fe₅₀Mn₂₅Al₂₅₋ₓGaₓ with x= 0, 2.5, 5.0, 10.0) are listed in table 1.
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<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>As cast Fe(<em>{50})Mn(</em>{25})Al(_{25})</td>
<td>SF1</td>
</tr>
<tr>
<td>2</td>
<td>As cast Fe(<em>{50})Mn(</em>{25})Al(<em>{22.5})Ga(</em>{2.5})</td>
<td>SF2</td>
</tr>
<tr>
<td>3</td>
<td>As cast Fe(<em>{50})Mn(</em>{25})Al(<em>{20})Ga(</em>{5})</td>
<td>SF3</td>
</tr>
<tr>
<td>4</td>
<td>As cast Fe(<em>{50})Mn(</em>{25})Al(<em>{17.5})Ga(</em>{7.5})</td>
<td>SF4</td>
</tr>
<tr>
<td>5</td>
<td>As cast Fe(<em>{50})Mn(</em>{25})Al(<em>{15})Ga(</em>{10})</td>
<td>SF5</td>
</tr>
<tr>
<td>6</td>
<td>Annealed Fe(<em>{50})Mn(</em>{25})Al(_{25})</td>
<td>ASF1</td>
</tr>
<tr>
<td>7</td>
<td>Annealed Fe(<em>{50})Mn(</em>{25})Al(<em>{20})Ga(</em>{5})</td>
<td>ASF3</td>
</tr>
<tr>
<td>8</td>
<td>Annealed Fe(<em>{50})Mn(</em>{25})Al(<em>{15})Ga(</em>{10})</td>
<td>ASF5</td>
</tr>
</tbody>
</table>

*Table 6.1* Acronyms of samples of the as cast and annealed Fe\(_{50}\)Mn\(_{25}\)Al\(_{25-x}\)Ga\(_{x}\) (x = 0, 2.5, 5.0, 7.5, 10.0) Heusler alloys.

### 6.2.2 Material Characterizations

The structure of the ingots have been characterized by means of XRD using PANalytical Empyren instrument with CuK\(_\alpha\) (\(\lambda = 1.5406 \text{ Å}\)) radiation in Bragg-Brentano para-focusing geometry. The XRD measurement has been performed in continuous scan mode at 45kV and 30mA at a scan rate of 0.013\(^\circ\) in the range 20 from 10 – 110\(^\circ\). SEM (QUANTA 200) has been used in order to study the surface morphology and chemical composition of the alloy operated at 25 kV equipped with the secondary electron detector, back scattered electron detector and energy dispersive X-ray spectrometer. Hardness measurements of all the samples were done with the help of METCO HMV-2T microhardness tester at different loads. The tests were conducted up to a load till cracks were observed around the indentation impression. The calibration of micro-indenter was carried out with the help of standard hardness test block having 700 VHN provided with the instrument. The standard diamond pyramid shape Vickers indenter provided with the equipment was used.

### 6.3. RESULTS AND DISCUSSION

#### 6.3.1 Structural properties of Fe\(_{50}\)Mn\(_{25}\)Al\(_{25-x}\)Ga\(_{x}\) Heusler alloys

**6.3.1.1 XRD Measurements**

The full Heusler alloys with stochiometric composition X\(_2\)YZ crystalize L\(_2\)_1, B2 and A2 structures with space group Fm-3m, where X and Y belongs to the transition
elements and Z is nonmagnetic main group element. The primitive and conventional cell of full Heusler alloys with L2₁-type crystal structure comprises with four interpenetrating fcc sublattices with atoms at X₁ (0.25, 0.25, 0.25); X₂ (0.75, 0.75, 0.75); Y (0.5, 0.5, 0.5); and Z (0, 0, 0) as illustrated in Fig. (1). In perfectly ordered state the chemical structure of Fe₂MnAl is full heusler alloys with lattice constant 5.816Å (s.g. Fm-3m). Mn and Al atoms occupies the X₂ and Z crystallographic sites respectively and the two equivalent sites (designated as X₁ and Y) are occupied by Fe atoms in the crystal structure. Every Fe atom is surrounded by four Mn and four Al atoms as first nearest neighbors whereas; each Mn atom has eight Fe as first nearest neighbors that forms a face-centered cubic (fcc) arrangement. Thus it is evident from Fig. (1) that in the structure Fe atoms occupy the 8c Wyckoff position at (0.25, 0.25, 0.25) sublattices, Mn and Al atoms located at 4b (0.75, 0.75, 0.75) and 4a (0, 0, 0) sublattices respectively. For the Ga substituted alloys the Ga and Al atoms are assumed to randomly occupy the 4a site (0, 0, 0).

![Image of Fe₂MnAl Heusler alloy structure](image)

**Fig. 1** Primitive cell and conventional cell of Fe₂MnAl Heusler alloy.

The intensity of reflections from the different planes is proportional to the square of the structure factor (F²). In case of X₂YZ Heusler compounds, the chemical ordering of Y and Z atoms is reflected by (111) lattice plan. (200) reflections coincide with the superlattice reflections of X atom, whereas; (2 2 0) is order-independent principal reflections (Webster, 1969). Fig. 6.2(a) illustrate the calculated XRD pattern of Fe₂MnAl sample (a = 5.816Å) for ordered L₂₁ Heusler structure (Buschow et al., 1981). The experimental XRD patterns of the SF1 (Fe₂MnAl) and SF5 (partially Ga
substituted Fe$_{50}$Mn$_{25}$Al$_{15}$Ga$_{10}$ samples have been presented in Fig.1 (b-c). As anticipated, the absence of (111) peak pointed out the great disorder in the occupation of Mn and Al atoms. The ordering in the Fe sublattice become visible due to the presence of (200) superlattice diffraction peak. Few peaks of the face centered tetragonal (FCT) phase were also present with parent (L2$_1$) phase in SF1 and SF5 samples.

Fig. 6.2 (b-f) shows the X-ray diffraction patterns of Fe$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ ($x=0, 2.5, 5.0, 7.5, 10.0$) alloys measured at room temperature. The characteristic reflections obtained from the samples were found in accordance to what was described above. The X-ray diffraction analysis of SF1 sample reveals the presence of ordered L2$_1$ structure along with some minority phase of face centered tetragonal (S.G. P4/mmm) structure. The existence of (111) and (200) lattice reflections and their relation with the (220) reflection provides the rough estimation of the degree of atomic ordering. More is the

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![X-ray diffraction patterns](image)

**Fig. 6.2** (a) Calculated XRD pattern of Fe$_2$MnAl, Experimental XRD patterns of (b) SF1, (c) SF2, (d) SF3, (e) SF4 and (f) SF5 Heusler alloys
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The intensity of these reflections indicate the evolution of more ordered crystal structure. As the Ga content increases, the intensity of (220) reflection first decreases sharply for SF2 and SF3 samples and then increases for SF4 (Fig. 6.2). The (200) diffraction peak was observed for the samples with $x \leq 7.5$. In comparison to (220) diffraction peak, the intensity of (200) peak was very low which gives the signature for the existence of a certain degree of disorder between the Fe and Al/Ga atoms in the structure (Wurmehl et al., 2005; Du et al., 2013; Hongzhi et al., 2007). The (200) reflection was found to be missing for the SF5 sample (Fig. 6.2(f)).

The XRD pattern of annealed alloys has been shown in Fig. (6.3). The absence of (111) and (200) diffraction peaks revels that on annealing the structural ordering decrease remarkably. The diffraction peak (220) associated with order independent principle reflection get sharper for all the annealed alloys. The peak intensity of the minority phase (FCT) in the ASF5 sample increases remarkably due to increase in the volume fraction of the FCT phase. However, the higher angle peaks ((400) and (422)) becomes broader with increase in Ga content Fig. 6.3(a-c). Hence the present

![Powder XRD patterns of (a) ASF1, (b) ASF3, and (c) ASF5 Heusler alloys](image)

**Fig. 6.3** Powder XRD patterns of (a) ASF1, (b) ASF3, and (c) ASF5 Heusler alloys
investigation suggests that annealing deteriorates the structural perfection. However annealing of CoFeCrGe Heusler alloys ribbons evaluates the tetragonal phase (Jina et al., 2018). It is difficult to assess the degree of ordering from the observed X-ray diffraction intensities because of the weak superlattice reflections (Umetsu et al., 2014). Although there are other sophisticated techniques such as he synchrotron radiation, which can bring a better understanding of the order-disorder degree in the structure. A systematic increase in the lattice parameter from \(a=5.82 \text{ Å} \) (\(x=0\)) to 5.84 Å (\(x=10\)) was observed from the powder XRD data for the as-cast alloys (see table 6.2). Moreover, on annealing an increase in the lattice parameter has been estimated from the powder XRD data than that of as cast alloys (see table 6.2). This variation in the lattice parameter may be associated with the difference in the atomic size (radius) of Ga (1.36 Å) and Al (1.18 Å). Due to the variation in the lattice parameter with increasing Ga content (around 1% with increase in the value of \(x\)), a significant change in the density of states (DOS) at the Fermi level can be expected.

The variation in the lattice parameter ‘\(a\)’ for as cast alloys as a function of Ga content was shown in Fig. (6.4) for both as cast and annealed alloys. A very small shift in the diffraction peaks towards the lower angle side was noticed by increasing the Ga content (Fig (6.2, 6.3)). Similar behavior was observed in the case of Fe\(_2\)MnSi alloy, where Si was substituted by Ge (Zhang et al. 2003). Moreover Gd addition in NiMnGa give raise the modulated structure (Zhang et al. 2003b). It can be seen from Fig. (6.4) that the lattice parameter increases linearly with increase in the Ga content which is in agreement with the Vegard’s law (Zhang et al., 2003). Moreover, there was no signature of the crystal structure transformation with substitution of Ga. There are two main factors which may be responsible for the change in the degree of atomic ordering and variation in the lattice parameter; (i) atomic radius and (ii) the surface energy of substituent Ga. Both Ga and Al are trivalent but Ga has larger atomic radius while surface energy is half than that of Al (Vegard et al., 1921). Therefore the partial substitution of Al by Ga might result in lowering the surface energy of the Fe-Mn-Al(Ga) alloy system. In the case of Ga substitution up to 5 at% (\(x=5.0\)) the first factor (atomic radius) dominates over the second factor (surface energy), and therefore the intensity of the main XRD peaks decreases due to atomic disordering. As we further increase the Ga content, the surface energy dominates over the atomic radius. Hence on
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Variation of lattice parameter 'a' with Ga content of as cast and annealed \(Fe_{50}Mn_{25}Al_{25-x}Ga_x\) (\(x=0, 5.0, 10.0\)) Heusler alloys (The straight line is the linear fit to the data)

Crystallization sharp increase in the XRD peak intensity along the (220) plane was observed.

The larger atomic radius and lower surface energy of the substituent (Ga) in comparison to Al causes a change in the lattice parameter and hence variation in the crystallite size and strain. Table 6.2 depicts the lattice parameters, crystallite size and lattice strain of the all samples estimated by X-ray diffraction data for as-cast and annealed alloys. The larger peak width for the Ga substituted alloys can be evident from Fig. (6.2). The variation in the crystallite size and strain was supposed to be responsible for this peak broadening. The crystallite size of as cast alloys first increases from ~ 21 nm (for x=0) to ~ 36 nm (for x=5) and then decreases to ~ 20 nm (for x=10). Similar pattern has been followed by the annealed alloys (see table 6.2). This indicates that for a particular amount of Ga substitution the crystal structure becomes more ordered. Similar variation (first increase and then decrease) in the lattice strain has been observed for the other alloys. This shows the relaxation in the strain for the alloys with...
higher Ga content (SF4 and SF5). The strain was found to be minimum for the SF4 alloy. This again increases for the SF5 alloy, because of the existence of minor FCT phase.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Structure</th>
<th>Cry. Size (nm)</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF1</td>
<td>5.827</td>
<td>4.925</td>
<td>L2₁</td>
<td>21.5</td>
<td>0.11</td>
</tr>
<tr>
<td>SF2</td>
<td>5.833</td>
<td>----</td>
<td>L2₁</td>
<td>26.4</td>
<td>0.37</td>
</tr>
<tr>
<td>SF3</td>
<td>5.840</td>
<td>----</td>
<td>L2₁</td>
<td>36.4</td>
<td>0.38</td>
</tr>
<tr>
<td>SF4</td>
<td>5.842</td>
<td>----</td>
<td>L2₁</td>
<td>22.0</td>
<td>0.09</td>
</tr>
<tr>
<td>SF5</td>
<td>5.846</td>
<td>4.927</td>
<td>L2₁</td>
<td>20.9</td>
<td>0.16</td>
</tr>
<tr>
<td>ASF1</td>
<td>5.838</td>
<td>----</td>
<td>L2₁</td>
<td>27.1</td>
<td>0.17</td>
</tr>
<tr>
<td>ASF3</td>
<td>5.859</td>
<td>----</td>
<td>L2₁</td>
<td>27.1</td>
<td>0.17</td>
</tr>
<tr>
<td>ASF5</td>
<td>5.881</td>
<td>4.930</td>
<td>L2₁</td>
<td>19.1</td>
<td>0.13</td>
</tr>
</tbody>
</table>

*Table 6.2* Lattice parameters (a, c), structure, crystallite size and strain for the as cast and annealed Fe₅₀Mn₂₅Al₂₅₋ₓGaₓ (x= 0, 2.5, 5.0, 7.5, 10.0) Heusler alloys.

6.3.1.2 SEM Measurements

Figure 6.5 shows the typical SEM secondary electron images of Fe₅₀Mn₂₅Al₂₅₋ₓGaₓ (x=0, 2.5, 5.0, 7.5, 10.0) alloys. All the alloys show the exhibits the columnar microstructure with coherent planer interface and characterized by the column width. The diversity in the columnar structure (shape and width) is clearly visible and width ranging from 9.92 μm to 14.90 μm. such columnar structure was formed due to the large temperature difference from the lower surface contact with the water cooled side of the tube to the upper surface. The preferred crystallographic orientation is indicated by the arrow, shown in Fig. 6.5(a-e), which is also the direction of the solidification. The presence of holes in the inter granular location was observed in the Ga substituted alloys Fig. 6.5(b-e). The size of the holes in the Ga substituted alloys was increasing from SF2, Fig. 6.5(b) to SF5, Fig. 6.5(e) samples gives a signature of enhanced brittleness. The reason of increase in the brittleness of the alloys is presence of Ga in the alloys. It is known that p electron of Ga has a very strong covalent interaction with d electron of Fe atom, which produces an ordering of the atom occupation and thus
Fig. 6.5 SEM secondary electron images of (a) SF1, (b) SF2, (c) SF3, (d) SF4 and (e) SF5 alloys.

enhances the intrinsic brittleness of the samples with increase in Ga concentration. Thus we can conclude that the brittleness is increasing with Ga content.

In order to get the information of the elemental distribution on the surface of the alloys elemental line scanning has been performed. The line scanning profile recorded from the columnar microstructure of all samples (SF1 to SF5) has been shown in Fig. 6.
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6(a-e). The homogeneous distribution with respect to distance, of the constituents is evident from the Fig. (6.6). The EDS line scanning profile obtained from the four different areas for each sample gives the signature that the Ga contain was increasing whereas, Al concentration was decreasing from SF1 to SF5 sample which is an expected sign of stoichiometry in the present investigation.

![Fig. 6.6 The line scanning profile of (a) SF1, (b) SF2, (c) SF3, (d) SF4 and (e) SF5 Heusler alloys.](image)

In order to check the purity of the samples the EDX measurements have been performed for each Fe₅₀Mn₂₅Al₂₅₋ₓGaₓ (x=0, 2.5, 5.0, 7.5, 10.0) alloys. The peaks associated with the constituent only, appears in the spectra confirms the purity of the alloys under investigation Fig. (6.7). The EDX spectra was calculated at least from the four regions in every sample and the average of that has been given in the table (Fig. 6.7(f)) for individual samples. This confirms that the composition was very close to stoichiometry.
6.3.2 Mechanical properties of Fe$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ Heusler alloys

6.3.2.1 Indentation Measurements

Microindentation measurements are performed for Fe$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ (x= 0, 5.0, 10.0) alloys at the test load between 25g to 1000g using Vickers diamond indenter. The Vickers microhardness (H) has been calculated in GPa units by employing the following relationship (Mukhopadhyay et al., 2001)

$$H = 1.854 \times 9.8 \times \frac{P}{d^2} \quad \text{…… (6.1)}$$

Where $d$ is the average diagonal length of the Vickers indentation impressions in µm and $P$ is the indentation test load (g). The dependence of hardness value on the indentation test load for SF1, SF3 and SF5 samples are shown in Fig. (6.8). Each data
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Fig. 6.8 Variation in hardness (VHN) with respect to load (g) for SF1, SF2 and SF3 Heusler alloys.

Point in the plot is an average of at least five measurements at each applied test load. It is evident from the hardness versus load characteristic curves that with increasing the load the hardness decreases due to indentation size effect (ISE) (Pharr et al., 2010; Sahin et al., 2005; Sahin et al., 2007; Kölemen et al., 2006; Mukhopadhyay et al., 2006). However, there was initial increase in the hardness values at lower load of indentation and this may be due to relatively smaller amount of plastic deformation vis-à-vis that of elastic component. The hardness values at 300 g for the SF1, SF3, and SF5 samples were found to be ~3.53, ~9.14 and ~9.36 GPa respectively.

6.3.2.2 Meyer’s law

To determine the ISE, the most widely used empirical equation that uses the correlation technique between the test load ‘P’ and the resultant indentation size ‘d’ by employing a simple power law known as Meyer’s law and is given by

\[
P = k.d^n \quad \text{(6.2a)}
\]
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$$\log P = \log k + n \log d \quad (6.2b)$$

Where ‘k’ is the material constant or power fit constant and is related to the resistance of metal to penetration. The exponent ‘n’ is the size-effect index, also known as Meyer’s index and usually considered as a measure of ISE. The experimental indentation data obtained for the samples in the present study was plotted in Fig. (6.9). The linear relationship can be seen from the figure which suggests that the Meyer’s law was appropriate to delineate the indentation data. The best-fit values for the parameters k and n were calculated by linear regression analysis and the results were summarized in table (6.3). The obtained values for n gives the higher apparent hardness values at

![Graph showing linear regression analysis of logP vs logd according to Meyer's law.](image)

**Fig. 6.9** Linear regression analysis of logP vs logd according to Meyers law.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>n</th>
<th>k (kg/µm^n)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF1</td>
<td>2.14</td>
<td>1.85</td>
<td>0.988</td>
</tr>
<tr>
<td>SF3</td>
<td>2.12</td>
<td>1.58</td>
<td>0.989</td>
</tr>
<tr>
<td>SF5</td>
<td>2.26</td>
<td>1.67</td>
<td>0.983</td>
</tr>
</tbody>
</table>

**Table 6.3** Regression analysis results of experimental data according to Equation (2a).
lower loads suggest the existence of ISE. But this classical Meyer’s law was found to be inadequate in describing the origin of ISE (Armstrong et al., 2006; Gong et al., 2000). Thus to get the basic understanding of ISE some new method is needed.

6.3.2.3 PSR Model

‘Li and Bradt’ have tried to give an explanation for the ISE by employing the “Proportional Specimen Resistance” (PSR) model (Li et al., 1993; Li et al., 1996; Sahin et al., 2008). According to this model, there are two factors that are liable for decrease in the hardness value with increase in test load. In this model, the applied test load, ‘P’ is related to the indentation diagonal length ‘d’ through a polynomial relationship as follows:

\[ P = a_1d + a_2d^2 \]  \hspace{1cm} (6.3a)

where the parameters \( a_1 \) and \( a_2 \) are constants for a given material and can be related with the elastic and the plastic properties of the test material, respectively. The parameter \( a_1 \) is related to the ISE contribution and measures the surface effect during the microhardness indentation. Particularly, \( a_2 \) is supposed to be measure of “true hardness; “\( H_{psr} \). In the case where the nanoindentation test is performed with Vickers indenter, the value of \( H_{psr} \) can be directly calculated from \( a_2 \) with relation:

\[ H_{psr} = \frac{P - a_1d}{(26.43)d^2} = \left( \frac{a_2}{26.43} \right) \]  \hspace{1cm} (6.4)

According to equation (3b) the plot \( P/d \) vs \( d \) should be a straight line and the parameters \( a_1 \) and \( a_2 \) can be easily obtained from the intersection point and slope of the curve, respectively. In the present investigation the plot \( P/d \) vs \( d \) was found to be remarkably non-linear Fig. (6.10(a)), suggesting that Eq. (3b) did not provide the accurate description for ISE for the present samples because the PSR model suggests that the \( a_2 \)-term in Eq. (3b) may be measure of the load-independent hardness (\( H_{Li} \)). Every material has only one characteristic value of the load-independent hardness (\( H_{Li} \)) while in present investigation for each sample, different \( a_2 \)-values may be obtained (Fig. 6.10(a)) if the ISE is calculated in different range of applied test load. Therefore it can be concluded that the present PSR model not give a satisfactory explanation of the ISE of the examined samples. Many reports shows the failure of this model for single
Effect of Ga substitution on the phase stability of crystal (Sahin et al., 2005; Sahin et al., 2008), some cobalt based alloys (Sangwall et al., 2003) and for several ceramics (Gong et al., 2000; Gong et al., 1999).

6.3.2.4 MPSR Model

Gong et al. have proposed a modified PSR (MPSR) model to study the ISE behavior of several materials (Stevenson et al., 2002). The MPSR model is defined as follows

\[ P = a_0 + a_1d + a_2d^2 \]

(6.5)

Where \( a_0 \) is a constant related to the residual surface stresses associated with the surface grinding and polishing during the sample preparation. The parameters \( a_1 \) and \( a_2 \) are the same constants as defined in PSR model. Therefore the values of the constants \( a_0, a_1 \) and \( a_2 \) can be estimated by plotting the \( P(d) \) data as \( P(\text{kg}) \) vs \( d(\mu\text{m}) \) plot. The applications of equation (5) for all the samples (SF1, SF3 and SF5) examined in the present investigation are shown in Fig. (14). The solid lines in this joining the data points in plots were obtained by a conventional polynomial regression according to equation (5). Evidently, the above equation (5) is proven reasonably suitable for the delineation of the experimental data. Similar to the PSR model, the load-independent hardness \( (H_{mpsr}) \) can be estimated directly from the best-fit value of the \( a_2 \) from the plot Fig. (6.10(b)) and is given by

\[ H_{mpsr} = \frac{P - a_0 - a_1d}{(26.43)d^2} = \left( \frac{a_2}{26.43} \right) \]

(6.6)

The estimated best-fit values of the parameters \( (a_0, a_1 \) and \( a_2 \) included in equation (5) and corresponding \( H_{mpsr} \) values for each sample have been listed in table (6.4).

It is well known that the parameter \( a_0 \) in Eqs. (5) and (6) is a specimen constant, instead of material constant. This parameter is dependent on the surface finishing process used in the preparation of the sample as well as on the material properties too. The relatively smaller negative values of \( a_0 \) in Table 6.4 seem to be reasonable estimations of the magnitudes of the residual surface stresses for the test samples (SF1, SF3 and SF5), which have been subjected to a careful polishing followed by grinding. The parameter \( a_1 \) represents the surface contribution to the indentation hardness and changes from one crystal growth direction to another. Actually this variation in the \( a_1 \) values belongs to the differences in the surface contributions to the indentation.
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Fig. 6.10 (a) Plot P/d vs d according to PSR model, (b) Plot P vs d according to MPSR model, (c) Variation of $a_0$ with $a_1/a_2$ ratio, (d) Variation in the yield strength with Ga content.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$a_0$ (kg)</th>
<th>$a_1$ (kg/µm)</th>
<th>$a_2$ (kg/µm$^2$)</th>
<th>$H_{mps}$ (GPa)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF1</td>
<td>-31.4570</td>
<td>6.0280</td>
<td>0.1118</td>
<td>4.23</td>
<td>0.9991</td>
</tr>
<tr>
<td>SF3</td>
<td>-14.1548</td>
<td>7.9680</td>
<td>0.2986</td>
<td>11.29</td>
<td>0.9986</td>
</tr>
<tr>
<td>SF5</td>
<td>-0.6387</td>
<td>4.9163</td>
<td>0.3967</td>
<td>15.01</td>
<td>0.9974</td>
</tr>
</tbody>
</table>

Table 6.4 Regression analysis results of experimental data according to Equation (5)

hardness for different crystal growth directions (Sahin et al., 2007; Kaji et al., 2002; Stevenson et al., 2002).

Li and Bradt have investigated that the parameters $a_1$ and $a_2$ can be related to the elastic and plastic properties of the test material respectively. The magnitude of the material parameter $E/H$ is measure of the indentation residual stress arising from the
disequilibrium of the plastic zone and the surrounding elastic matrix (Lawn et al., 1980). Similarly, the \( a_1/a_2 \) values may be treated roughly as a measure of the residual stresses caused due to grinding and polishing of the sample. Figure (6.10(c)) shows a strong correlation between the \( a_0 \) and the \( a_1/a_2 \) values. This gives the impression to be an indirect support for the above discussion.

The fundamental mechanical properties of the test material describe its response on indentation and hence certain basic mechanical properties of the material can be extracted from the hardness test. For instance, both the tensile test and the hardness test measures the resistance of a metal to plastic flow, and the outcomes of these tests may very similar to each other. Because of relatively nondestructive nature and experimental ease the hardness test is preferred. From a simple hardness measurement, the possibility to calculate the yield strength or the tensile strength is very appealing. By utilizing the hardness value the yield strength \( \sigma_y \) can be calculated as follows (Cahoon et al., 1971):

\[
\sigma_y = \left( \frac{H_{\text{mpsr}}}{2.9} \right) \left[ 1 - (n - 2) \right] \left[ 12.5 \frac{n - 2}{1 - (n - 1)} \right]^{n^{-2}} \quad \text{(6.7)}
\]

For Meyer’s index \( n > 2 \)

If \( n \leq 2 \) the equation (7) reduces to \( \sigma_y = \frac{H_{\text{mpsr}}}{3} \) (Pal et al., 2003). In the present experimental observation the value of \( n \) is greater than 2, therefore equation (7) has been employed to calculate the yield strength. It is well known that a slip system (composed of dense atomic arrays) will be formed from a slip direction, called the close packed and slip planes having high atomic density. By twinning and slip the deformation takes place on these slip systems. The value of estimated yield strength increases from 1.386 GPa to 5.627 GPa with increase in the crystal growth along the (220) plane. The estimated \( \sigma_y \) values for different Ga content reveals the linear nature as shown in Fig. (6.10(d)). Thus it can be concluded that with increase in Ga content the \( \sigma_y \) increase in the present investigation.

6.4 CONCLUSIONS

On the basis of the detailed investigation on the structural and mechanical properties of Fe\(_{50}\)Mn\(_{25}\)Al\(_{25}\)\(_x\)Ga\(_x\) (\( x = 0, 5.0, 10.0 \)) alloys following conclusions can be drawn.
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(1) The XRD outcomes showed that these alloys are formed in the ordered L$_2$$_1$ phase (s.g. Fm-3m) while Ga free alloy possesses some minority FCT phase along with L$_2$$_1$ phase. The crystallite size first increases with Ga content then decreases for higher Ga (X=10) content alloy.

(2) The lattice parameter of the ordered L$_2$$_1$ phase is slightly greater than that of the stoichiometric Fe$_2$MnAl alloy and increases linearly with Ga substitution.

(3) The brittleness increases with increase in Ga content in place of Al. Based on the observations, a comprehensive study of hardness measurements of investigated alloys were conducted employing various existing models, i.e. the classical Meyer’s law, Li and Bradt’s proportional specimen resistance model (PSR), the modified proportional specimen resistance model (MPSR).

(4) No fruitful information about the origin of ISE can be obtained by the Meyer’s law. However, it yields a good fit for the measured indentation data.

(5) While investigating for relatively wider range of test loads, the estimated ISE cannot be described with PSR model as the graph was not linear.

(6) The load independent hardness values estimated by employing MPSR model for SF1, SF3 and SF5 specimen were 4.23 GPa, 11.29 GPa and 15.01 GPa respectively. The values of the yield strength for different growth directions and varied from 1.386 GPa to 5.627 GPa.