CHAPTER 6

EFFECT OF Si SUBSTITUTION ON THE ORDERING OF $Ni_3Fe$ AND SITE SUBSTITUTION EFFECTS IN $Mi_3Fe_{1-x}Si_x$ ALLOYS
6.1. INTRODUCTION

There have been several studies undertaken to understand the effect of ternary additions on the hyperfine field systematics [1-3] and L1_2 ordering behaviour of the Ni_3Fe alloy [4,5]. In the L1_2 ordered Ni_3Fe structure Fe atoms occupy the cube corner sites and have 12 Ni first neighbours (at the face centre sites) and 6 Fe second neighbours (at cube corners). Addition of Cr to Ni_3Fe was found to reduce the number of Fe atoms on Ni sites thereby increasing the degree of L1_2 order, and the presence of Cr on a Ni first neighbour site decreased the Fe field by 45 kOe [1]. Studies with Sn, Al, and Mn substitutions showed that these substituents primarily occupy the Fe site and increase the L1_2 ordering temperature. This tendency was empirically understood in terms of the heat of solution of metal B in metal A, when A and B form an A_B alloy since both dissolution of metal B in A and L1_2 ordering lead to breaking of B - B bonds and their replacement by A - B bonds [2].

The heat of solution of Si in Ni is large (1530 meV) and the ordering temperature of Ni_3Si is also large (1423 K) [6]. In this work we therefore study the effect of Si addition to Ni_3Fe which has not been experimentally studied as yet. We look at the site substitution behaviour of Si, hyperfine field perturbation at Fe due to presence of Si and the near neighbour effects due to L1_2 ordering, through a Mössbauer effect and X-ray diffraction study of the Ni_3Fe_{1-x}Si_x quasi-binary system.
6.2. EXPERIMENTAL

$\text{Ni}_3\text{Fe}_{1-x}\text{Si}_x$ alloys in the composition range $x = 0.0, 0.1, 0.25, 0.5, 0.75$ and 0.9 were prepared by arc melting. Requisite quantities of 4N purity iron, nickel, and silicon powders were mixed thoroughly and pressed into pellets. They were melted under argon atmosphere in an arc furnace with a water cooled copper hearth. Melting was done repeatedly to ensure homogeneity. The typical weight loss in the melting process was 2%. The alloy ingots were homogenised at 800° C for 48 hours after sealing them in quartz tubes under a pressure of about 10 torr. A part of homogenised alloy ingot was filed to coarse powder and subsequently ground to finer powder in mortar and pestle. The powders were annealed at 475° C for 7 days in vacuum sealed quartz tubes ($\approx 10$ torr). Mössbauer absorbers (having natural Fe content of 25 mg/cm$^2$) were prepared from alloy powders after mixing with boron nitride. The homogenised ingots of $X = 0$ and 0.25 were splat quenched in an Edmund Bühler ultra quenching apparatus to prepare the disordered alloys.

Samples were characterised by powder X-ray diffraction on a Siefert Isodebyeflex Model 2002 X-ray diffractometer using CuK$_\alpha$ radiation. Room temperature $^{57}$Fe Mössbauer spectra were recorded on $\mu$P based spectrometer [7]. A $^{57}$Co in Rh matrix source was used. The spectra were analysed using a Fast Fourier Transform (FFT) program. The Mössbauer spectrum for $x = 0.75$ showed two resolved six line patterns. The six line pattern due to the lower field was about double the intensity of the pattern due to the
higher field. The FFT program could not fit this complex spectrum. Thus this complex spectrum was fitted using a stripping procedure [8].

6.3. RESULTS AND DISCUSSION

6.3.a. X-ray Diffraction

The powder X-ray diffraction patterns for all the compositions \(0 \leq x \leq 0.9\) could be indexed to a fcc unit cell and the lattice parameter \(a\) was calculated using Bradley and Jay plots [9]. The value of \(a\) was calculated for each line in the X-ray pattern with indexed \(hkl\) values and were plotted against \(\cos^2 \theta\). By the extrapolation of \(a\) vs. \(\cos \theta\) plot to \(\theta = 90^\circ\), the intercept on the ordinate gave the exact value of \(a\). The variation of \(a\) with Si concentration \(X\) is shown in Fig. 6.1. The value of \(a\) for \(\text{Ni}_3\text{Fe}\) comes out to 3.54 Å and it is in good agreement with the reported value. The reported value of \(a\) for \(\text{Ni}_3\text{Si}\) is indicated by a solid circle. For \(x = 0.75\) composition, there is indication of an extra phase but the diffraction peaks were not well resolved for this extra phase. However presence of this extra phase was clearly observed in the Mössbauer spectrum because Mössbauer technique is very much sensitive to the presence of small amount of any phase. The hyperfine field value for this extra phase was calculated from the Mössbauer spectrum using stripping procedure. This hyperfine field value coincides with the value for \(\alpha\)-Fe. It indicates that there is a precipitation of \(\alpha\)-Fe at this composition. For \(x = 0.9\) we got a single phase alloy
Fig. 6.1. Variation of lattice parameter \( a \) for fcc unit cell with Si concentration \( x \) in \( \text{Ni}_3\text{Fe}_x\text{Si}_{1-x} \) system. Solid circle represents the value for \( \text{Ni}_3\text{Si} \) taken from ref. 12.
and the value of \( a \) is close to \( \text{Ni}_3\text{Si} \) value. These observations shows that \( \text{Ni}_x\text{Fe} \) and \( \text{Ni}_3\text{Si} \) were not miscible throughout the composition range and there exist a miscibility gap around \( x = 0.75 \) composition. Based on the above arguments the ternary phase diagram for this alloy system is drawn. Fig. 6.2 shows the ternary phase diagram and miscibility gap around \( x = 0.75 \) composition. The numbers 1, 2, 3, 4, 5 and 6 represent \( x = 0, 0.1, 0.25, 0.5, 0.75 \) and 0.9 respectively. The region C indicates the miscibility gap and solid circle is for \( x = 0.75 \). These results are qualitatively similar to those of \( \text{Ni}_x\text{Fe}_1-x\text{Al} \) alloy system which shows a miscibility gap near \( x = 0.5 \) composition [10].

6.3.b. **Hyperfine Fields, Linewidths and Magnetic Dilution Effects**

Fig. 6.3 shows the Mössbauer spectra for the splat quenched alloys of compositions \( x = 0 \) and 0.25. The average hyperfine field for the \( \text{Ni}_3\text{Fe} \) alloy (\( x = 0 \)) is 292.7 kOe and the linewidth of the outermost lines is 0.63 mm/sec. The average field and linewidths of outer lines obtained by Drijver et. al [4] for cold rolled foils was 295.7 kOe and 0.75 mm/sec respectively. The effect of increasing order by annealing at 760 K is a decrease in average field (approaching a value of 272 kOe, which is the field observed at Fe in Ni metal) and also a decrease in linewidth. The decrease in field as well as linewidth is correlated to the \( \text{L}_1^2 \) long-range order in the system. Although the average field for the partially ordered samples are seen to fit this dependence very well, the data on cold rolled foils of Drijver et. al are not consistent with this dependence. This is attribu-
Fig. 6.2. Quasi-binary section of the phase diagram for \( \text{Ni}_3\text{Fe}_{1-x}\text{Si}_x \) alloy system. C indicates the approximate region of the miscibility gap.
Fig. 8.3. Mössbauer spectra for splat quenched alloys: $\text{Ni}_3\text{Fe}$ (a), and $\text{Ni}_3\text{Fe}_{0.75}\text{Si}_{0.25}$ (b). The solid lines are fits to data using Fast Fourier Transform Program.
ted to the possible change in microstructure of the foils due to cold rolling. The parameters obtained from our rapid anvil and piston quenching should be better representative of the state of high chemical disorder in the samples. Similarly the field obtained for our ordered foils is 281 kOe which is slightly higher than the value of 278 kOe obtained by Drijver et. al for their ordered samples. The linewidths obtained is slightly lower (0.44 mm/sec for our alloys as compared to 0.45 to 0.46 mm/sec for Drijver et. al) suggesting that the final degree of order achieved is also slightly better in our alloy. The average hyperfine field for the splat quenched $\text{Ni}_3\text{Fe}_75\text{Si}_{25}$ alloy observed to be 260.8 kOe and the linewidth of outer lines is 0.63 mm/sec. There is thus a large decrease ($\approx 32$ kOe) in hyperfine field at Fe site due to the presence of Si first near neighbours which arise in the disordered sample due to random occupying of all sites by Fe, Si and Ni. This field shift to be compared with dilution effects observed by Stearns [11] in bcc Fe-Si alloys. A decrease of 8 percent field at Fe was observed due to presence of Si first neighbours at a distance of 0.87 $a_{\text{Fe}}$ in the bcc system. For Si in fcc $\text{Ni}_3\text{Fe}$, the first neighbour Fe – Si distance is also about 0.87 $a_{\text{Fe}}$ but the field decrease observed is 11 percent as compared to the field in disordered $\text{Ni}_3\text{Fe}$.

6.3.c. Chemical Ordering Effects

The effect of chemical ordering (anneal at $475^\circ$ C for 7 days) on the $\text{Ni}_3\text{Fe}_75\text{Si}_{25}$ alloy is to increase the average hyperfine field to 271.3 kOe, a value which is close to the value
of Fe hyperfine field in nickel (272 kOe). This shows that the chemical order induced in the system is also of L1_2 type with Si atoms occupying the Fe sites, thereby producing a first neighbour environment of Fe consisting of 12 Ni atoms (face centres) and a second neighbour environment consisting of Fe and Si atoms (at cube corners). The magnitude of hyperfine magnetic field is lower than that obtained for ordered Ni_3Fe (281 kOe) which is also consistent with the presence of nonmagnetic Si neighbours at Fe sites in the second neighbour shell.

The effect of the ordering heat treatment (anneal at 475°C for 7 days) on all samples is shown in Fig. 6.4 and the average hyperfine field values are shown in Fig. 6.5. Drijver et al. deduced linear correlation between Fe hyperfine field and number of first near neighbour (n_1) and second near neighbour Fe (n_2) atoms as follows:

$$H = H(0,6) + n_1 \Delta H_1 + (n_2 - 6) \Delta H_2$$

(6.1)

where $H(0,6) = 276.6$ kOe is the field for 0 first and 6 second neighbour Fe atoms (fully ordered L1_2 structure), $\Delta H_1 = 11.6$ kOe is the field contribution due to one Fe first neighbour and $\Delta H_2 = 2.7$ kOe is the contribution due to one second Fe neighbour. Based on Eq. (6.1), the hyperfine field at Fe site in fully ordered Ni_{1-x}(Fe, Si)_x samples with Si substituting Fe atoms in second neighbour sites and acting as ‘magnetic holes’ in the lattice will be, as shown by the dotted line in Fig. 6.5. The experimental value of hyperfine field for our ordered sample for
Fig. 6.4. Mössbauer spectra for ordered $\text{Ni}_3\text{Fe}_{1-x}\text{Si}_x$ alloys of various compositions subjected to the ordering heat treatment as discussed in text. Solid lines are the fits (for all compositions except $x = 0.75$) to the data using Fast Fourier Transform Program. For $x = 0.75$ composition, a stripping procedure as discussed in Chapter 4 was employed to get the fields corresponding to Fe rich and Ni rich phases.
Fig. 6.5. Observed variation of average hyperfine field $H_{hf}$ in the Ni$_2$Fe$_3$ Si alloy system. The dashed line is the expected variation for a fully ordered system according to the model of Drijver et al [4].
\( x = 0.25 \) is in agreement with the expected value for a well ordered sample. The linewidth of the outermost lines for this sample is observed to be 0.47 mm/sec which is close to the value expected for a well ordered sample. At higher Si concentration \( (x = 0.5) \) the hyperfine field value is much smaller than that expected from a simple dilution approach and this large decrease is due to presence of Si atoms which can be also present in the first neighbour shell if the ordering is not complete. This is also borne out by the very large linewidth (0.93 mm/sec) for the sample. Beyond this composition, the \( x = 0.75 \) alloy shows phase decomposition (Fe rich \( \text{Ni}_3\text{Si} \) and \( \alpha\text{-Fe} \)) and a predominantly \( \text{Ni}_3\text{Si} \) phase at \( x = 0.9 \). This corroborates the X-ray diffraction data discussed earlier.

6.4. CONCLUSIONS

Although \( \text{Ni}_3\text{Fe} \) and \( \text{Ni}_3\text{Si} \) both crystallize in an fcc structure there exists a miscibility gap around \( x=0.75 \) composition in the quasi binary \( \text{Ni}_3\text{Fe}_{1-x}\text{Si}_x \) system. The field reduction at Fe site due to presence of Si first neighbours is slightly larger (11 \%) in the fcc \( \text{Ni}_3\text{Fe} \) system as compared to the field reduction (8\%) due to Si first neighbours in the bcc Fe-Si alloy. Ordering treatment of splat quenched \( \text{Ni}_3\text{Fe} \) and \( \text{Ni}_3\text{Fe}_{0.75}\text{Si}_{0.25} \) alloys gives \( \text{L1}_2 \) order with only Fe and Si second neighbours to Fe sites suggesting that Si atoms show preferential substitution of Fe sites.
REFERENCES