A Mössbauer effect study of $Ni_3Fe_{1-x}Si_x$ alloys for $0 \leqslant x \leqslant 0.9$

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[57]Fe Mössbauer effect studies were carried out on the quasibinary $Ni_3Fe_{1-x}Si_x$ alloy system for $x = 0$, 0.1, 0.25, 0.5, 0.75 and 0.9 compositions. Single phase alloys are formed upto $x = 0.5$ whereas a two phase alloy is observed for $x = 0.75$ composition. The $x = 0.9$ composition also shows single phase formation with lattice parameters close to Ni_3Si. Substitution of Si primarily takes place at the Fe sites and the $x = 0.25$ composition shows a high degree of $L1_2$ order. The magnetic hyperfine field systematics are discussed in terms of first and second neighbour configurations.

1. Introduction

It is observed that a third element added to a binary alloy system exhibiting chemical order–disorder transformations can have a pronounced effect on its properties such as ordering temperatures, kinetics of ordering, the state of final order achieved, domain structures, etc. [1–3]. The technologically important alloys formed in the binary Ni–Fe alloy system have been extensively studied for their chemical ordering behaviour, its' influence on magnetic properties and on the magnetic hyperfine field behaviour in going from disorder to order states [4, 5]. The chemical ordering in Ni_3Fe alloy is, however, very sluggish, the final degree of order achieved is not high, and several studies have been carried out by adding ternary elements to it to look for hyperfine field systematics, change in ordering temperature, the site at which the third element substitutes, etc.

The structure into which Ni_3Fe orders is the $L1_2$ structure which has Fe atoms sitting at the corner sites and Ni atoms at face centred sites. Krolas [6] studied the problem of adding a third element to Ni_3Fe from the point of view of bond energies and heats of formation of alloys. He observed that the chemical ordering tendency such as ordering temperature in an alloy (e.g. A_3B ordering alloys such as Ni_3Fe) is related to the heat of formation of B in A because the ordering process is effectively the same as breaking B–B bonds and replacing them by A–B bonds. A good correlation between ordering temperature and heats of solution of B in A was observed by considering several elements such as Al, Ge, Ga, Mn, Pt, Si, Cr, Sn etc. Krolas also showed empirically that the addition of a third element, C, to A_3B alloy will raise its ordering temperature if the B–C bonds have a higher repulsive bond energy relative to B–B bonds, because this would favour A–C bonds (ordering) more than B–C bonds. The heat of solution of Si in Ni metal is high ($147\ kJ\ mol^{-1}$) and the Si–Fe bond energy, as deduced by Krolas [6], is $3.47\ kJ\ mol^{-1}$ (repulsive) which is

three times as large as compared to Fe–Fe bond energy. The Si atoms are therefore expected to occupy Fe sites (avoiding Fe–Si bonds) and also give higher ordering temperatures.

In this study we look at the addition of Si to Ni_3Fe which has not been experimentally studied as yet. We look at the site substitution behaviour of Si in Fe_3Si to check the model of Krolas [6]. We study the hyperfine field perturbations due to Si neighbours, the systematics of hyperfine field at Fe site due to chemical order–disorder transformations and the effect of Si on the degree of order achieved. The technique of Mössbauer spectroscopy is used in conjunction with X-ray diffraction for these studies.

2. Experimental techniques

$Ni_3Fe_{1-x}Si_x$ alloys for the composition $x = 0.0$, 0.1, 0.25, 0.5, 0.75 and 0.9 were prepared by arc melting. Requisite quantities of 4 N 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 performed repeatedly to ensure homogeneity. The typical weight loss in the melting process was 2%. The alloy ingots were homogenized at 800 °C for 48 h after sealing them in quartz tubes under a pressure of about 10^{-2} Pa. A part of the homogenized alloy ingot was filed to coarse powder and subsequently ground to finer powder in a mortar and pestle. The powders were annealed at 748 K for 7 days in vacuum sealed quartz tubes ($\approx 10^{-2}$ Pa). Mössbauer absorbers (having natural Fe content of $25\ mg\ cm^{-2}$) were prepared from alloy powders after mixing with boron nitride. The homogenized ingots of $x = 0$ and 0.25 were splat quenched in an Edmund Bühler ultra rapid-quenching apparatus to prepare the disordered alloys.

Samples were characterized by powder X-ray diffraction on a Siefert Isodebyeflex Model 2002 X-ray

diffractometer using CuK_{α} radiation. Room temperature ^{57}Fe Mössbauer spectra were recorded on μP 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]. The typical errors in the determination of hyperfine field values are ± 0.05 T.

3. Results and discussion

The powder X-ray diffraction patterns for all the compositions ($0 \leqslant x \leqslant 0.9$) could be indexed to a f.c.c. 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 h.k.l. values and were plotted against $\cos^2 \theta$. By the extrapolation of a versus $\cos^2 \theta$ plot to $\theta = 90°$, the intercept on the ordinate gave the exact value of a. The variation of a with Si concentration x is shown in Fig. 1. The value of a for Ni_3Fe comes out to 0.354 nm and it is in good agreement with the reported value. The reported value of a for Ni_3Si 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, the presence of this extra phase was clearly observed in the Mössbauer spectrum, because the Mössbauer technique is very much more sensitive to the presence of a small amount of phase. The hyperfine field value for this extra phase was calculated from the Mössbauer spectrum using a stripping procedure. This hyperfine field value coincides with the value for α-Fe. It indicates that there is a precipitation of α-Fe at this composition. For $x = 0.9$ we got a single phase alloy and the value of a is close to Ni_3Si value. These observations show that Ni_3Fe and Ni_3Si were not miscible throughout the composition range and there

Figure 2 Mössbauer spectra for splat quenched Ni_3Fe (a) and $Ni_3Fe_{0.75}Si_{0.25}$ (b).

exists a miscibility gap around $x = 0.75$ composition. These results are qualitatively similar to those of $Ni_3Fe_{1-x}Al_x$ alloy system which shows a miscibility gap near $x = 0.5$ composition [10].

Fig. 2 shows the Mössbauer spectra for the splat quenched alloys of compositions $x = 0$ and 0.25. The average hyperfine field for the Ni_3Fe alloy ($x = 0$) is 29.3 T and the linewidth of the outermost lines is 0.63 mm s^{-1}. The average field and linewidths of outer lines obtained by Drijver et al. [4] for cold rolled foils were 29.6 T and 0.75 mm s^{-1}, respectively. The effect of increasing order by annealing at 760 K was a decrease in average field (approaching a value of 27.2 T, which is the field observed at Fe in Ni metal) and also a decrease in linewidth. The decrease in field as well as linewidth was correlated to the $L1_2$ long-range order in the system. Although the average field for the partially ordered samples were seen to fit this dependence very well, the data on cold rolled foils of Drijver et al. were not consistent with this dependence. This was attributed to a possible change in microstructure of the foils due to cold rolling. The parameters obtained from our rapid anvil and piston quenching should be more representative of the state of high chemical disorder in the samples. Similarly the field obtained for our ordered foils is 28.1 T which is slightly higher than the value of 27.8 T obtained by Drijver et al. for their ordered samples. The linewidths obtained are slightly lower (0.44 mm s^{-1} for our alloys as compared to 0.45 to 0.46 mm s^{-1} 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 $Ni_3Fe_{0.75}Si_{0.25}$ alloy is observed to be 26.1 T and the linewidth of outer lines is 0.63 mm s^{-1}. There is thus a large decrease (≈ 3.2 T) in hyperfine field at Fe site due to the presence of Si first near neighbours which arise in the disordered sample, owing to random occupancy of all sites by Fe, Si and

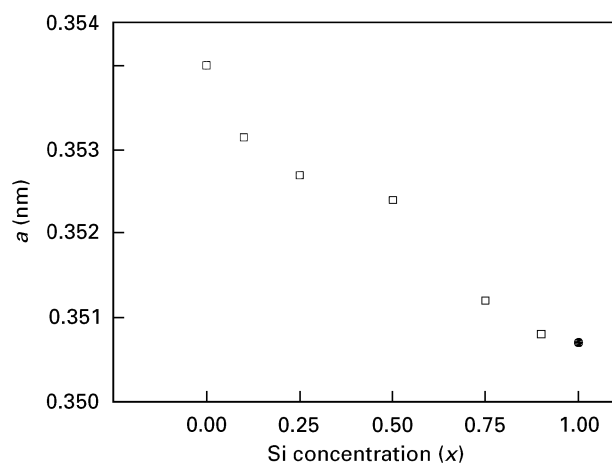*Figure 1* Variation of lattice parameter for f.c.c. unit cell with Si concentration x in $Ni_3Fe_{1-x}Si_x$ system. Solid circle represents the value for Ni_3Si taken from [12].
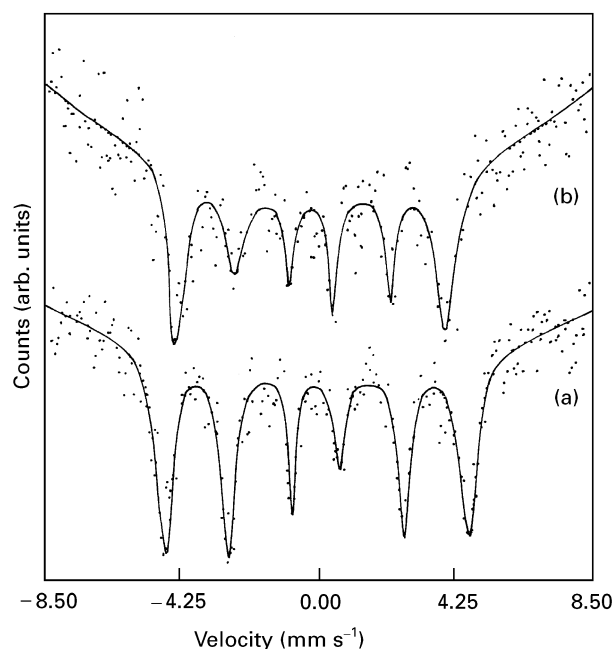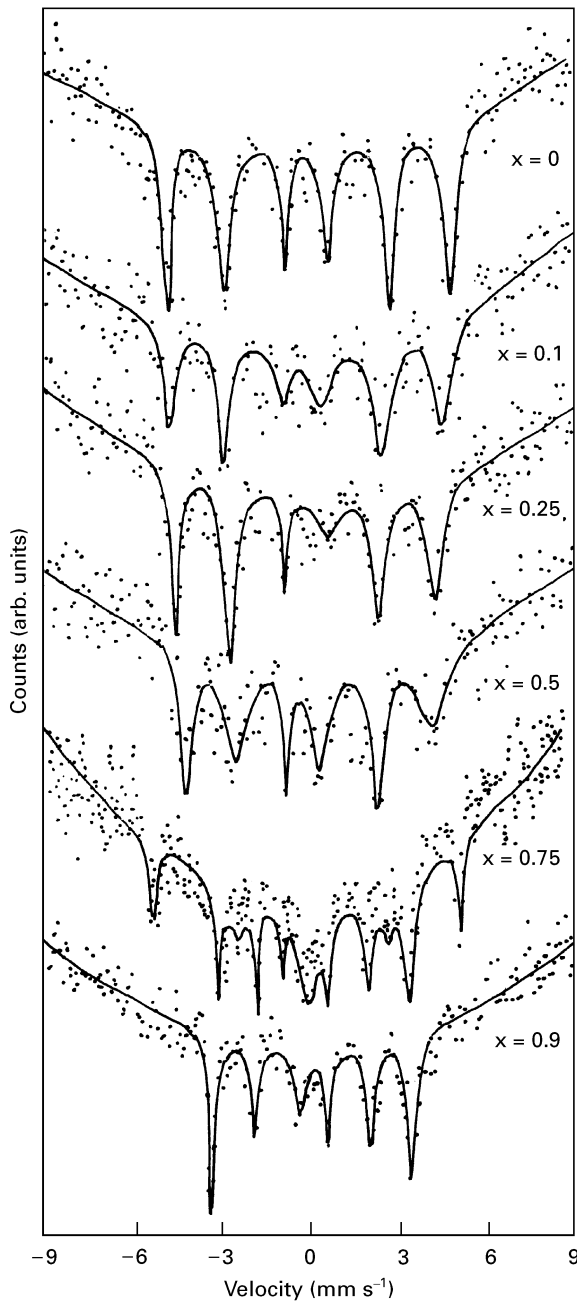
Figure 3 Mössbauer spectra for ordered $Ni_3Fe_{1-x}Si_x$ alloys of various compositions subjected to the heat treatment as discussed in the text.

Figure 4 Observed variation of average hyperfine field, $\bar{H}_{hf}$, in the $Ni_3Fe_{1-x}Si_x$ alloy system. The dashed line is the expected variation for a fully ordered system according to the model of Drijver et al. [4]. $\square$, ordered alloys; $\blacksquare$, disordered alloys.

Ni. This field shift should be compared with the dilution effects observed by Stearns [11] in b.c.c. Fe–Si alloys. A decrease of 8 % field at Fe was observed because of the presence of Si first neighbours at a distance of 0.87 a_{Fe} in the b.c.c. system. For Si in f.c.c. Ni_3Fe, the first neighbour Fe–Si distance is also about 0.87 a_{Fe} but the field decrease observed is 11%, as compared to the field in disordered Ni_3Fe.

The effect of chemical ordering (anneal at 748 K for 7 days) on the $Ni_3Fe_{0.75}Si_{0.25}$ alloy is to increase the average hyperfine field to 27.1 T, a value which is close to the value of Fe hyperfine field in nickel (27.2 T). 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
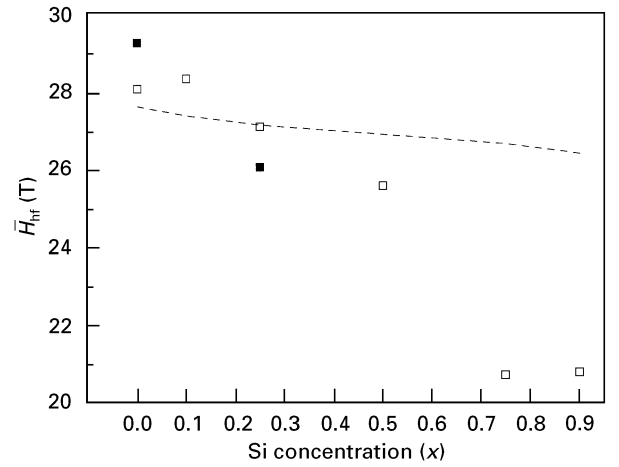
a second neighbour environment consisting of Fe and Si atoms (at cube corners). The magnitude of the hyperfine magnetic field is lower than that obtained for ordered Ni_3Fe (28.1 T) which is also consistent with the presence of non-magnetic Si neighbours at Fe sites in the second neighbour shell.

The effect of the ordering heat treatment (anneal at 748 K for 7 days) on all samples is shown in Fig. 3 and the average hyperfine field values are shown in Fig. 4. Drijver et al. [4] deduced linear correlation between the Fe hyperfine field and the number of first near neighbour (n_1) and second near neighbour Fe (n_2) atoms as follows

$$H = H(0,6) + n_1\Delta H_1 + (n_2 - 6)\Delta H_2 \qquad (1)$$

where $H(0,6) = 27.66$ T is the field for 0 first and 6 second neighbour Fe atoms (fully ordered $L1_2$ structure), $\Delta H_1 = 1.16$ T is the field contribution with one Fe first neighbour and $\Delta H_2 = 0.27$ T is the contribution with one Fe second neighbour. Based on Equation 1, the hyperfine field at Fe site in fully ordered $Ni_3(Fe_{1-x}Si_x)$ samples with Si substituting for Fe atoms in second neighbour sites and acting as "magnetic holes" in the lattice would be as shown by the dotted line in Fig. 4. The experimental value of hyperfine field for our ordered sample for $x = 0.25$ 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 s^{-1} 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; this large decrease is because of the 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 s^{-1}) for the sample. Beyond this composition, the $x = 0.75$ alloy shows phase decomposition (Fe rich Ni_3Si and α-Fe) and a predominantly Ni_3Si phase at $x = 0.9$. This corroborates the X-ray diffraction data discussed earlier.

4. Conclusions

1. Although Ni_3Fe and Ni_3Si both crystallize in a f.c.c. structure there exists a miscibility gap around $x = 0.75$ composition in the quasi-binary $Ni_3Fe_{1-x}Si_x$ system.

2. The field reduction at an Fe site due to presence of Si first neighbours is slightly larger (11%) in the f.c.c. Ni_3Fe system as compared to the field reduction (8%) due to Si first neighbours in the b.c.c. Fe–Si alloy.

3. Ordering treatment of splat quenched $Ni_3Fe_{0.75}Si_{0.25}$ alloy gives $L1_2$ order with only Fe and Si second neighbours to Fe sites suggesting that Si atoms show preferential substitution of Fe sites.

Acknowledgements

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