MÖSSBAUER SPECTROSCOPY OF Fe-Ni ALLOYS

SAMI H. MAHMOOD, FUAD H. RAWWAGAH,
ABDEL-FATTAH LEHLOOH AND SABRI MAHMOUD
Yarmouk University, Irbid, Jordan

Abstract

We report the results of structural and Mössbauer studies of the alloy system Fe$_{1-x}$Ni$_x$ (0.2≤x≤0.61). X-ray diffraction results show that the alloy with x=0.2 has a bcc structure, and that with x≥0.37 has an fcc structure. However, the alloys with x=0.30 and 0.35 contain both bcc and fcc structures. Mössbauer study confirms the structural results and indicates that the alloys with 0.39≤x≤0.50 contain a paramagnetic phase in addition to the ferromagnetic α-bcc and γ-fcc phases. This paramagnetic phase is associated with the low spin γ-fcc phase; it is a metastable state that appears as a first step toward the conversion form the bcc to the fcc phase as x increases.

Introduction

Iron-Nickel binary alloys had been investigated using magnetic(1-6), Mössbauer(6-18) and diffraction studies(4-8). In particular, the famous Invar alloys, which contain 30 to 40 at. % Ni, had been subjected to various studies since the discovery of its zero thermal expansion coefficient at room temperature in 1897(1) (Dumpich et al., 1987) In addition, Invar alloys exhibit other anomalies(2,3) (Rancourt et al., 1987; Wohlfarth, 1979), such as instability of ferromagnetism, low Curie temperature and saturation magnetizations, large high field susceptibilities, relatively flat magnetization versus temperature... etc.

X-ray diffraction indicates that the system passes from an α-bcc to a γ-fcc phase as x increases, and that the two phases co-exist for intermediate concentrations(4,6) (Dumpich et al., 1987). Other studies revealed that alloys with 20-50 at. % Ni have a tendency to split into two fcc phases, γ and γ', and the Invar effect was attributed to the two fcc states of iron.(7) (Kaufman, 1963).
Mössbauer measurements show that the average hyperfine field $H_{hf}$ for the alloys with bcc structure is between 330 and 340 koe, and that it decreases from 310 to 261 koe with increasing Ni content for the alloys with fcc structure (Jartych et al., 1992). Also, it was reported (Rancourt et al., 1989) that the invar alloys Fe$_{65}$Ni$_{35}$ contains three distinct phases; the high-spin $\gamma$-fcc matrix (ferromagnetic below 500 K), and precipitates of the high-spin $\alpha$-bcc (ferromagnetic below 1000 K) and the low-spin $\gamma'$-fcc phases. Further, it was found that the hyperfine field has a minimum value in the region of concentration between 30 and 40% Ni. In this study we use x-ray diffraction and Mössbauer Spectroscopy to examine the structural and magnetic properties of Fe-Ni alloys prepared by chemical co-precipitation. To our knowledge, this is the first time these alloys are prepared using this method.

2- Experimental

The alloys were prepared using chemical co-precipitation (Charles, 1980). Stock solutions of ferric nitrate and nickel acetate were prepared and the volumes of the solutions required to prepare a given alloys sample were mixed together to form a homogeneous mixture of the two solutions. A pH of ~ 7 for the new solution is reached by adding ammonia solution. The metal ions in the mixture are precipitated by adding a solution of ammonium carbonate, $(NH_4)_2 CO_3$. The precipitate is filtered by suction, washed by distilled water and dried in air for ~12 hours at 100°C. The dry metal carbonate mixture is powdered and placed in a catalytic fixed bed flow reactor through which air was passed at a flow rate of 150 cm$^3$/min. and a temperature of 520°C for one hour. The produced homogeneous metal oxide mixture is then reduced in a hydrogen gas atmosphere at 520°C for five hours, and the resulting alloy powder is cooled to room temperature by an electric fan for about an hour, under helium atmosphere.
The structure of the alloys was investigated by X-ray diffraction using a standard 0-2θ diffractometer with Co-Kα (λ=1.79025 Å). Mössbauer absorbers were prepared on a piece of tape, and the spectra were collected over 512 channels using a standard constant acceleration Mössbauer spectrometer with a source of Co⁵⁷ in Palladium. The sextet spectrum of α-Fe was used to calibrate the system, and the shifts in the absorption lines of the samples are measured relative to the centroid of this spectrum. The spectra were fitted using standard routines, and the broad magnetic spectra were fitted by a distribution of hyperfine fields using 40 sextet components.

3- Results

3.1 Crystal Structure

The recorded diffraction patterns of the alloys with x=0.20, 0.30, 0.35, 0.37, 0.50, and 0.61, are shown in Fig. 1. The results of the structural analysis indicate that the sample with x=0.20 is a single phase of the bcc type, and the samples with x≥0.37 are single phase of the fcc type. However, the patterns for the samples with x=0.30 and 0.35 show the peaks corresponding to the two phases. The indices for the various peaks are shown in the diffraction patterns. The lattice parameter for the bcc phase (a=2.87 Å) is similar to that for pure Fe. However, comparing the lattice parameter for the fcc phase (a=3.59 Å) with that of pure Ni (a=3.52 Å), we find a 2% expansion in the fcc cell. This could be due to the fact that the Fe atom has a larger radius than the Ni atom.

It is not possible to detect atomic ordering in these alloys using x-ray diffraction because of the closeness of the atomic scattering factors, f_A and f_B, of Fe and Ni atoms, and the fact that the intensity of the superstructural (100) reflection is proportional to |F|² ∝ |f_A - f_B|².
3.2 Mössbauer Spectroscopy (MS)

Room temperature Mössbauer spectra for the alloy system are shown in Fig. 2. The spectra of the samples with $x=0.20$ and 0.61 show only magnetically split patterns, whereas the spectra of the samples with $0.30 \leq x \leq 0.50$ show a magnetically split component and a central paramagnetic line. The paramagnetic line starts to appear with low intensity at $x=0.30$, and at $x=0.35$ it becomes more intense and the magnetic lines shrink drastically. As $x$ is increased slightly to $x=0.37$, a significant drop in the intensity of the paramagnetic line is observed, concomitant with the phase transition from a mixed bcc-fcc state to a single fcc phase. As the nickel content is increased further the intensity of the paramagnetic line diminishes.

Mössbauer spectra are fitted according to the line shape of these spectra, and the fitting results are listed in Table 1. The spectrum of the sample with $x=0.20$ shows magnetic splitting with relatively sharp lines ($\Gamma=0.38$ mm/sec), and is therefore fitted with one sextet. The small broadening in the lines is attributed to the effect of alloying. The measured value of the hyperfine field ($H_{hf}=338$ koe) is in agreement with the results obtained by others ($6,9$) (Dumpich et al., 1987; Jartych et al., 1992). This value is attributed to the high spin $\alpha$-bcc phase.

The spectrum of the sample with $x=0.30$ shows magnetic splitting with relatively sharp lines, in addition to a weak central paramagnetic line and thus was fitted with a sextet and a singlet. The observation of a paramagnetic line in the spectrum of this sample is in agreement with MS results of Fe-Ni alloys containing 30 to 40 at.% Ni ($10$) (Chamberod et al., 1979). This line is attributed to the $\gamma'=fcc$ (low spin) phase. The hyperfine field for the sextet component is very close to that in the sample with $x=0.20$, and is thus attributed to the $\alpha$-bcc phase. These results are in agreement with our structural results which show an evidence of the presence of an fcc phase in addition to the dominant bcc phase.
The spectrum of the sample with $x=0.35$ exhibits a broad magnetically split component and a deep paramagnetic dip. This spectrum is similar to that observed by others for samples with similar Ni concentration\(^{10}\). In order to investigate the main features of the spectrum, it is first fitted by three components: two sextets corresponding to two magnetic sites, and a signlet corresponding to the $\gamma$-fcc phase (Fig. 3). The sextets with low and high hyperfine fields are attributed to the $\gamma$-fcc (high spin) phase and to the $\alpha$-bcc phase, respectively. This interpretation is consistent with the fact that the hyperfine parameters for the high field component are close to those for the spectrum of the sample with $x=0.20$, and that the sample with $x=0.35$ contains both bcc and fcc phases, as the x-ray data indicates.

The spectrum of the alloy with $x=0.37$ consists of a sextet with broad lines, and a paramagnetic line with intensity significantly less than that observed in the spectrum of the sample with $x=0.35$. The spectrum in fitted by one sextet and one signlet. The fitting parameters for the magnetic component are similar to those of the low field magnetic site of the previous sample, and thus, this component is attributed to the $\gamma$-fcc (high spin) phase. This result is in agreement with the x-ray data which show only fcc phase in this sample. Again, the paramagnetic line is attributed to the $\gamma$-fcc phase.

The spectrum of the sample with $x=0.50$ shows a broad sextet corresponding to the $\gamma$-fcc phase, and a weak paramagnetic line in the center. Finally the spectrum of the sample with $x=0.61$ is fitted with one magnetic component with hyperfine field corresponding to the $\gamma$-fcc phase.

The appreciable broadening in the spectral absorption lines of the magnetic components of the samples with $x \geq 0.35$ suggests that these alloys are atomically disordered. To account for this effect the spectra are fitted each by a distribution of fields, $P(H)$, and the results are shown in Fig.4. $P(H)$ for the sample with $x=0.35$.
shows a large peak at zero field belonging to the paramagnetic phase, and two peaks in the high field region belonging to the low field (fcc) and to the high field (bcc) sites. This result is consistent with the presence of three phases in this alloy. The ripples in the intermediate region can not be associated with real signals since they can not be distinguished from the scatter of the data. The single peak centered about the field corresponding to the $\gamma$-fcc phase in the high field region of $P$ ($H$) for the sample with $x \geq 0.37$ is consistent with the presence of one magnetic site with atomic disorder. The absence of the zero field peak in $P$ ($H$) for the sample with $x = 0.50$ could be due to the noise in the central region of the spectrum and to the small intensity of this line.

4. Discussion and Conclusions

X-ray diffraction study of the alloy system $\text{Fe}_{1-x}\text{Ni}_x$ prepared by the chemical co-precipitation have shown that the alloys with $x \geq 0.37$ are single phase of the fcc type and that with $x = 0.20$ is single phase of the bcc type. The alloys with $x = 0.35$ and 0.30 contain the two phases together. MS results confirm these observations, and indicate the presence of the low spin $\gamma$-fcc phase near the value $x = 0.35$. The variation of the intensity of the paramagnetic line with Ni concentration (Fig. 5) is an evidence that the occurrence of this phase is very sensitive to composition. This leads to the co-existence of the paramagnetic and the ferromagnetic phases due to local variation in the atomic environment around the Fe atom. Further, the results of MS indicate that as Ni concentration increases, the bcc phase starts to convert to the $\gamma$ phase, which then converts to the $\gamma$ phase with increasing $x$.

The relatively sharp absorption lines corresponding to the bcc phase indicate that the atomic environment of the Fe atoms are very similar, which could mean that this phase has some degree of atomic order. On the other hand, the absorption lines corresponding to the high spin fcc phase are obviously broad, especially in the
spectra which show appreciable paramagnetic line intensity. This is an evidence of the existence of appreciable variations in the atomic environment around the Fe atoms, indicating both the existence of atomic disorder and the sensitivity of the hyperfine field to atomic environment in this phase. This is consistent with the fact that as Fe-Ni experiences a phase transition from bcc to fcc with increasing Ni content it passes through a metastable γ-fcc (low spin) phase.

**Table (1)**

Fitting results for the spectra showing the hyperfine field (H_{hf}) in KOe, center shift (CS) in mm/sec, line width (Γ) (the outermost lines for the magnetic phases) in mm/sec, and the relative absorption area R for each phase.

<table>
<thead>
<tr>
<th>Magnetic site #1</th>
<th>Magnetic site #2</th>
<th>Paramagnetic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α-bcc</td>
<td>γ-fcc</td>
</tr>
<tr>
<td></td>
<td>X    H_{hf}     CS  Γ  R</td>
<td>H_{hf}     CS  Γ  R</td>
</tr>
<tr>
<td>0.20</td>
<td>337  0.00       0.38 1.00</td>
<td>-          -</td>
</tr>
<tr>
<td>0.30</td>
<td>340  0.02       0.40 0.90</td>
<td>-          -</td>
</tr>
<tr>
<td>0.35</td>
<td>339  0.02       0.44 0.23</td>
<td>305        -0.01   0.91 0.40</td>
</tr>
<tr>
<td>0.37</td>
<td>-      -         -    - 306   -0.02 0.94 0.90</td>
<td>-0.12      0.41      0.10</td>
</tr>
<tr>
<td>0.50</td>
<td>-      -         -    - 310   0.03 0.81 0.69</td>
<td>-0.09      0.40      0.04</td>
</tr>
<tr>
<td>0.61</td>
<td>-      -         -    - 305   -0.02 0.83 1.00</td>
<td>-          -          -</td>
</tr>
</tbody>
</table>
Fig. 1: X-ray diffraction patterns of the alloy system Fe$_{1-x}$Ni$_x$. 
Fig. 2: Mössbauer spectra of the alloys
Fig. 3: Mössbauer spectrum of the alloy Fe$_{0.65}$Ni$_{0.35}$
Fig. 4: Mössbauer spectra of the alloys fitted with distributions of hyperfine fields
Fig. 5: Dependence of the intensity of the paramagnetic component on the Ni content.
Notes


MÖSSBAUER SPECTROSCOPY OF Fe-Ni ALLOYS

References


