Mössbauer effect and XRD studies of iron–zinc binary alloys

R.G. Grant and D.C. Cook

Department of Physics, Old Dominion University, Norfolk, VA 23539, USA

Mössbauer spectroscopy and XRD were employed to characterize the microstructural properties of iron–zinc binary alloys between 0–31 at.% Fe. Samples were prepared with accuracies of ±0.5 at.% Fe, and the Mössbauer and lattice parameters were monitored as a function of iron concentration across each phase. Two iron sites were observed in the $\Gamma$ phase (18–31 at.% Fe), whose occupancies and isomer shifts varied continuously with iron content. However, the quadrupole splitting of each site remained constant. Within the $\Gamma_1$ phase (19–24 at.% Fe), three iron sites were observed whose isomer shifts and quadrupole splittings remained constant, while their occupancies varied with iron concentration. For the first time, a third iron site was observed in the $\delta$ phase (8–13 at.% Fe), whose occupancy increases with iron content. Also, the site occupancies of the two other $\delta$ sites appear to remain constant, while other Mössbauer parameters vary continuously with iron content. Analysis of the $\zeta$ phase (6–7 at.% Fe) showed the presence of one iron site, whose parameters were not observed to change due to the small variance in iron concentration. XRD studies indicate the lattice parameters across the $\Gamma$ and $\delta$ phases vary continuously with iron concentration. Moreover, a better understanding of these phases, as formed in galvanneal steel coatings, was obtained.

1. Introduction

Galvannealed coatings are comprised of iron–zinc alloy phases which have better corrosion resistance, particularly after painting, and are easier to weld than galvanized coatings. Annealing of the zinc-coated steel sheet allows the interdiffusion of zinc and iron, which forms an alloy coating comprised of up to four iron–zinc intermetallic phases ranging from the iron-rich $\Gamma$ phase, the $\Gamma_1$ and $\delta$ phases, and finally to the zinc-rich $\zeta$ phase. It is important to identify which phases form during the galvanneal process, understand the properties of each phase and know how to control the formation of any particular phase or phases in order to obtain optimum material performance. It has been the aim of this research to develop a data base of the crystalline and other microstructural properties of these iron–zinc intermetallics.

*Research supported by the International Lead Zinc Research Organization, Inc., Grant No. ZM-403 and Virginia’s Center for Innovative Technology, Grant No. MAT-92-007-01.

© J.C. Baltzer AG, Science Publishers
in order to aid the identification of the four phases formed in steel coatings. Particular emphasis has been placed on the variation in these properties as a function of iron concentration across each phase.

2. Preparation of iron–zinc intermetallics

The samples, indicated by dots in fig. 1, were prepared by thoroughly mixing carefully weighed amounts of high-purity, small-particle size iron and zinc powders and then pressing these powders under 50 tsi to form tablets. These were then encapsulated in an evacuated quartz tube and sintered at the appropriate temperature before quenching in liquid nitrogen in order to maintain the microstructural properties present at the particular sintering temperature. Following this, the tablets were crushed finely, encapsulated in another evacuated quartz tube and annealed at the sintering temperature for the same time as the original sinter. ICP and wet chemical titration techniques were used to determine the bulk composition of the samples to within ±0.5 at.% Fe.

3. Results

3.1. ZETA PHASE

The ζ phase spans a narrow iron concentration range between 5.9–7.1 at.% and has a peritectic melting point at 530 °C. It crystallizes in the monoclinic structure \( a \neq b \neq c, \beta \neq 90^\circ \), with space group C2/m [1], and has the stoichiometry FeZn_{13}. 
Fig. 2. Mössbauer spectra of a typical (a) $\zeta$, (b) $\delta$, (c) $\Gamma_1$, and (d) $\Gamma$ phase.

Three samples were prepared at two different iron concentrations, 6.40 and 7.04 at.%, within the $\zeta$ phase. The mean values of $a = 10.875$ Å, $b = 7.615$ Å, $c = 5.061$ Å and $\beta = 100.54^\circ$ lead to a unit cell volume of about 412 Å$^3$. The Mössbauer spectrum of a typical $\zeta$ phase intermetallic is shown in fig. 2(a), and consists of one very
small quadrupole split doublet, indicating that the iron is present in only one environment which crystallographically is nearly cubic. The lattice and Mössbauer parameters were found to remain constant as a function of iron concentration. This is probably due to the limited iron concentration range for this phase.

3.2. DELTA PHASE

The δ phase forms with iron concentration between 8.1–13.2 at.%. It has a peritectic melting point at 672 °C. It crystallizes in a hexagonal structure, $a = b \neq c$, $\gamma = 120^\circ$, with space group $P6_3mc$ [2]. The unit cell is very large, containing 555 atoms [3] and having a volume of 8228 Å$^3$. The lattice parameters $a$ and $c$ and the cell volume appear to decrease linearly and continuously with increasing iron content. The ratio of $c/a$ was found to be independent of iron concentration, indicating that the contraction of the unit cell with increasing iron content is isotropic; hence, no distortion of the unit cell is observed. The Mössbauer spectrum of a typical δ phase is shown in fig. 2(b). Analysis of the spectrum indicates the presence of three iron sites, labelled A, B, and C, which are purely quadrupole split. The isomer shifts of all three sites decreases gradually, but continuously, with increasing iron content, with those of the A and B sites being nearly identical. The quadrupole splittings of the A and B sites increase only marginally, whereas the quadrupole splitting of the C site increases rapidly with increasing iron concentration. This indicates that the crystal symmetry of the A and B sites remains constant across the δ phase, but that of the C site changes continuously. This supports the XRD data, which indicates a uniform expansion of the hexagonal lattice with increasing iron concentration. Relative areas of the subspectra, as shown in fig. 3(a), seem to indicate the occupancies by iron of the two main sites A and B decrease, while the occupancy of the C site increases with an increase in iron concentration. However, the ratio of the site occupancies of the two most populated iron sites remains constant at approximately 6:4. Therefore, the iron preferentially enters the C site, leaving the A and B sites at close to their initial occupancies. Perhaps the constant 6:4 ratio is suggestive of the octahedral and tetrahedral symmetries observed in the Γ structure, as will be discussed later.

3.3. GAMMA-1 PHASE

The Γ$_1$ phase forms between the iron concentrations of 18.9–24 at.%. It has a peritectic melting point at 550 °C and a nominal stoichiometry of Fe$_2$Zn$_{21}$. It crystallizes in a cubic structure with space group $F43m$ with 408 atoms per unit cell [4]. There does not appear to be any significant changes in the lattice parameter across the Γ$_1$ phase. The phase has an fcc crystal structure with a lattice parameter of approximately 17.977 Å. Figure 2(c) shows the Mössbauer spectrum of a typical sample within the Γ$_1$ phase. Spectral analysis shows the presence of three iron sites, A, B, and C, as we reported earlier [5]. The isomer shift and quadrupole splitting
are significantly different for each site, indicating that very different electronic and crystalline environments are present. Also, there are moderate changes in the Mössbauer parameters with iron concentration across the phase. This is in agreement with the XRD spectra, in which we see only a very small change in the lattice parameter with iron concentration. The quadrupole splittings and isomer shifts of the three iron sites remain nearly constant, while their populations vary continuously over a small range across the phase. This is not unexpected, since the atomic concentration in the fcc unit cell of this phase is significantly less than in the other phases.

3.4. GAMMA PHASE

The Γ phase forms between the iron concentrations of 18–31 at.%. It has a peritectic melting point at 782 °C and a nominal stoichiometry of Fe₂Zn₁₀. It crystallizes in the cubic γ-brass structure with space group 143m, and has 52 atoms per unit cell [6]. The lattice parameter changes linearly from approximately 8.97 Å to 9.01 Å as the iron concentration decreases from 30.24 down to 26 at.%. However, as the low iron concentration end of the Γ phase is approached, the lattice parameter asymptotes towards a constant value of 9.024 Å. The Γ structure consists of clusters
of 26 atoms located at the eight corners and body centered position of a bcc unit cell. Each cluster is identical and contains four crystallographically inequivalent sites, labelled inner tetrahedral, outer tetrahedral, octahedral and cubo-octahedral, which contain 4, 4, 6 and 12 atoms, respectively, per cluster. A total of 52 atomic sites are present in the bcc unit cell. Previous neutron diffraction studies [7] have been unable to conclusively ascertain which of the four sites are occupied by the iron atoms. Since more iron is observed to dissolve in this intermetallic than is found for other γ-brass binary alloys, it was thought that the iron was randomly distributing into all of the four sites. However, spectral fits indicate that only two of these four sites are occupied by iron atoms, as seen in fig. 2(d). The observation of only two iron sites and the values obtained for the fit parameters are in agreement with our previous studies [5]. We observe significant changes in the Γ spectra as a function of iron concentration. The quadrupole splittings of both sites exhibit small decreases with increasing iron concentration, indicating a marginal improvement in the cubic symmetry at the iron sites. Although the isomer shift of site B stays unchanged, the isomer shift of site A decreases continuously and quite rapidly with increasing iron concentration. Significant changes are observed in the relative areas of the two iron sites, as seen in fig. 3(b). As one approaches the high iron concentration end of the Γ phase, the relative areas, and thus the site occupancies, approach the ratio of 6:4. The fact that the changes in Mössbauer parameters are continuous across the Γ phase answers an important, long-standing question concerning the location of the iron atoms. Brandon et al. [6] produced a sample in the low iron end of the Γ phase and determined that the iron occupied only the inner tetrahedral and outer tetrahedral sites. On the other hand, Johansson et al. [7] produced a high iron concentration Γ sample and proposed that the iron occupied the inner tetrahedral and octahedral sites. Since we observe that the Mössbauer parameters change continuously, the above two explanations are incompatible. The relative areas of the two sites approach the limit of 6:4, indicating that the iron is occupying the inner tetrahedral and octahedral sites, in support of Johansson et al.

4. Conclusions

The Mössbauer and lattice parameters of both the δ and Γ phases vary continuously with iron concentration. However, the ζ and Γ₁ parameters do not change an appreciable amount as the percent of iron is varied. We attribute these moderate changes within the ζ and Γ₁ phases to the small variation in iron concentration across each phase. Furthermore, it is now possible to uniquely identify the δ and Γ₁ phases using XRD spectroscopy. Specifically, one can detect the presence of the Γ₁ phase in a δ sample and vice versa. Also, within the Γ phase the iron occupies the inner tetrahedral and octahedral configurations. Finally, the newly compiled data base of the microstructural properties of these binary alloys has aided in the study of galvannealed steel coatings.
References