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A Mössbauer study of Fe–Zn phases on galvanized steel

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Electron back-scattering Mössbauer spectroscopy has been used to examine the Fe–Zn intermetallic phases produced on galvanized steel. Spectra have been obtained from surfaces of the zeta, delta-prime (palisade), delta-prime (compact) and capital gamma phases, and these are discussed in terms of the crystal structure of each intermetallic phase.

1. Introduction

Back-scattering Mössbauer spectroscopy, whereby spectra are obtained by detecting the resonantly re-emitted γ-rays, X-rays, or low-energy conversion and Auger electrons, is proving to be a useful technique for studying surface layers on iron and its alloys [1]. The advantage of the back-scattering technique over the more conventional transmission Mössbauer spectroscopy is that one is not restricted to examining thin foils, since surface layers still attached to thick substrates can be examined. The electron back-scattering mode is particularly suitable for the examination of surface layers a few thousand Ångstroms thick, and to date several investigations have been published relating to the oxidation behaviour of iron [2–7]. Little Mössbauer work has been carried out, however, in the area of protective coatings. With respect to galvanized steel, Terrell [8] has presented an X-ray back-scattered spectrum from zinc-coated turbine blades, and Jones and Denner [9] a transmission spectrum of galvanized iron foil together with spectra of prepared Fe–Zn intermetallic phases. In the latter study, which was concerned with the kinetics of hot-dip galvanizing, a conclusive identification of the intermetallic phases was not attempted; such identification from transmission Mössbauer spectra is difficult because the large substrate iron peaks obscure the weak peaks due to the Fe–Zn phases. This problem has been eliminated in the present study by using electron back-scattering Mössbauer spectroscopy to examine separately each Fe–Zn intermetallic phase on galvanized steel.

2. Experimental

2.1. Specimen preparation

A thick galvanized coating on mild steel was produced by hot-dipping for 1 h at 455° C in an iron-saturated (0.03% Fe) zinc bath containing 0.5% lead. A metallographic section of the coating and a scanning electron micrograph of a fracture section are shown in Figs. 1a and b, where the various phases are indicated. Specimens with exposed surfaces of the zeta, ζ, delta-prime (palisade), δ_{1p} and delta-prime (compact), δ_{1k}, phases were prepared by mechanically polishing away the coating. After the Mössbauer spectrum of a particular phase had been recorded, the specimen was fractured and the thickness of the layer measured by scanning electron microscopy to ensure that only the surface of the phase in question was exposed. Because of the small thickness of the capital gamma, Γ, layer, and the non-uniformity of the steel/Γ layer interface (Fig. 1a), it was not possible to mechanically polish down to expose only the Γ layer. A specimen was obtained, however, by cooling a sample in liquid nitrogen and peeling off the complete coating; a Mössbauer spectrum was then taken of the underside of the Γ layer.*

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* A Mössbauer spectrum of the underlying steel surface indicated only a negligible amount of residual Γ layer.

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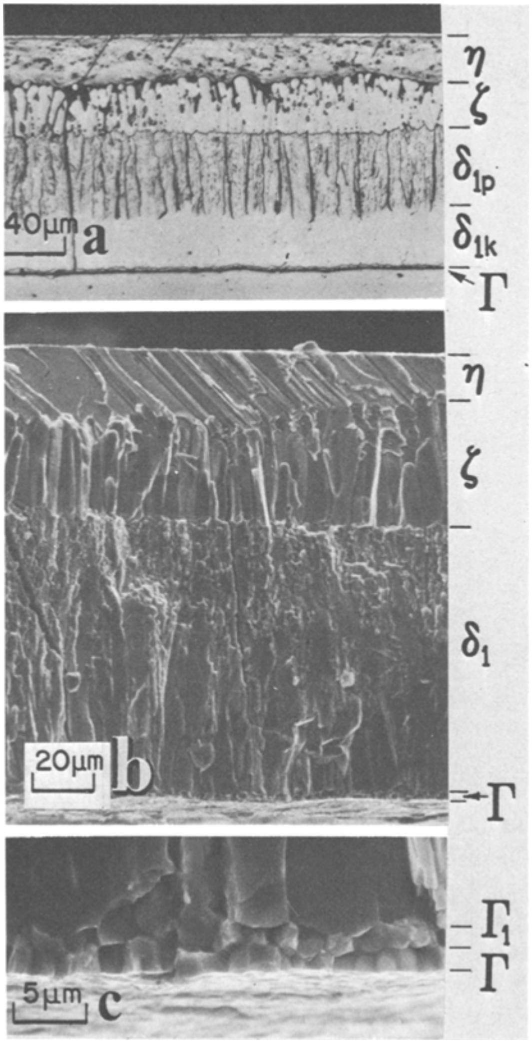

Figure 1 (a) Metallographic cross-section, and (b) scanning electron micrograph of a fractured section of the galvanized coating showing the "pure" Zn, η, layer and the Fe–Zn intermetallic phases. (c) Scanning electron micrograph of a fractured section showing the duplex nature of the Γ phase.

2.2. Mössbauer spectrometer

Mössbauer spectra were obtained at room temperature with a computerized constant acceleration spectrometer [10] using a 30 mCi Co^{57}/Pd γ-ray source. Specimens were mounted inside a proportional counter operating with a 96% He–4% CH_4 mixture so that the conversion and Auger electrons resonantly re-emitted from the intermetallic phase surface could be detected. Spectra were collected over the central 100 of 1024 velocity channels.

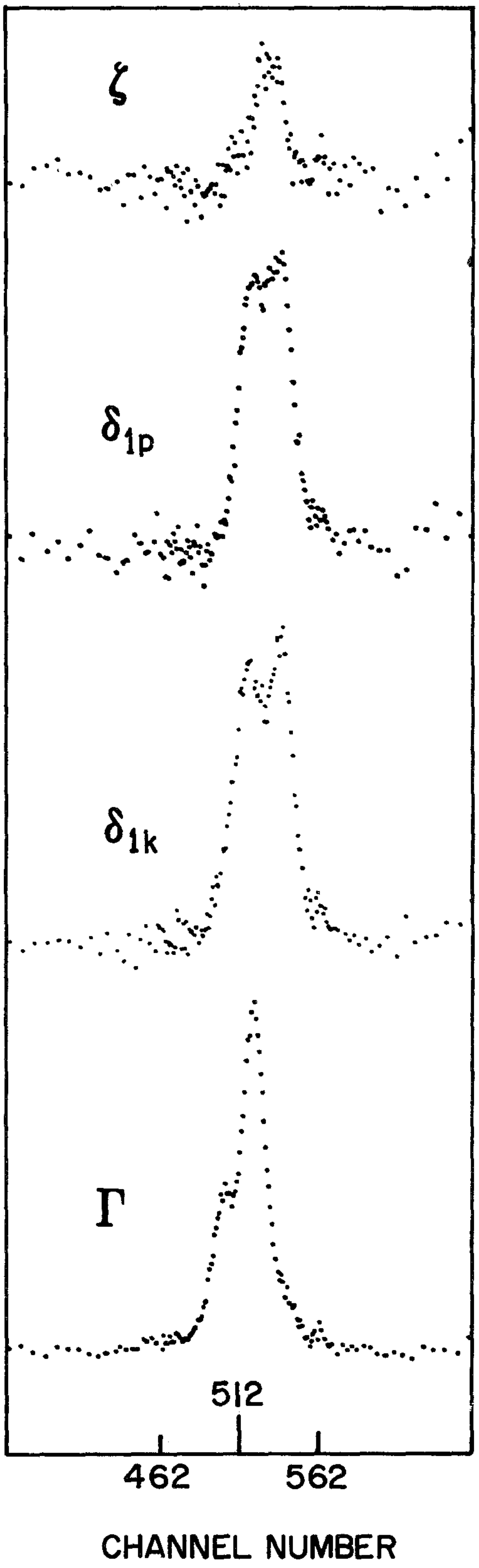

Figure 2 Electron back-scattering Mössbauer spectra of the Fe–Zn intermetallic phases on galvanized steel.

TABLE I Spectral parameters of the Fe–Zn intermetallic phases on galvanized steel

Phase	Isomer shift[a] (mm sec^{-1})	Peak 1/2 width (mm sec^{-1})	Peak splitting (mm sec^{-1})	Peak intensity ratio (Area[b]/Area[c])
ζ	0.49 ± 0.01	0.44 ± 0.04	–	–
δ_1 δ_{1p}	0.45 ± 0.01	0.41 ± 0.05[b] 0.39 ± 0.05[c]	0.38 ± 0.03	0.93 ± 0.16
δ_{1k}	0.42 ± 0.01	0.48 ± 0.02[b] 0.32 ± 0.02[c]	0.44 ± 0.01	1.45 ± 0.09
Γ	0.087 ± 0.002	0.30 ± 0.02[b] 0.36 ± 0.01[c]	0.41 ± 0.01	0.25 ± 0.02

[a] Relative to metallic Fe.
[b] Peak at lower channel number (velocity).
[c] Peak at higher channel number (velocity).

3. Results and discussion

The Mössbauer electron back-scattered spectra of the various Fe–Zn intermetallic phases are shown in Fig. 2. Peaks were computer fitted, based on Lorentzian line profiles, and the spectral parameters of the phases are given in Table I.

3.1. Zeta, ζ, phase

The equilibrium ζ phase, $FeZn_{13}$, has a monoclinic structure, and contains between 6.9 and 7.2 at% Fe [11–13]. According to Brown [14], the Fe atoms are surrounded by 12 Zn atoms at the vertices of a slightly distorted icosahedron, namely an approximately spherical shell of Zn atoms. (Electron microprobe analysis of galvanized coatings similar to those used in the present study [15] gave a 10% higher average Fe content and indicated that the Fe content increased slightly towards the ζ/δ_1 interface.) The spectrum of this phase, as seen in Fig. 2 comprises a broad peak of half-width 0.44 mm sec^{-1}. Somewhat similar spectra have been reported by Jones and Denner [9] and recently by Dunlop *et al.* [16] in transmission studies on synthetically prepared samples. In the latter study on partially enriched $FeZn_{13}$ (~ 10% Fe^{57}), the data best fitted a close quadrupole split doublet (splitting 0.15 mm sec^{-1}) of peak half-widths 0.25 mm sec^{-1} which is consistent with the known crystal structure. The isomer shift of 0.43 ± 0.01 mm sec^{-1} reported by Dunlop *et al.* [16] is smaller than the value of 0.49 ± 0.01 found in the present study.

3.2. Delta prime, δ_1, phase

The δ_1 phase (homogeneity range 8.1 to 13.1 at% Fe) is considered to have a crystal structure more complex than hexagonal with 555 ± 8 atoms per unit cell; the atomic positions are not known [11–13]. The phase, as seen in Fig. 1, comprises two structurally different layers: a palisade, δ_{1p}, layer and a compact, δ_{1k}, layer nearer to the steel interface. Controversy exists as to whether these layers are in fact two distinct phases. The layers behave differently towards chemical etchants, have different values of microhardness [17], and exhibit different diffusion behaviour [18]. Ghoniem and Löhberg [19] believe that the two δ_1 layers do represent separate phases having compositions corresponding to $FeZn_{10}$ (9.1 at% Fe) and $FeZn_7$ (12.5 at% Fe) often quoted in the literature [11]. They have proposed a modification of the phase diagram, and in agreement with this modification, electron microprobe analyses have shown that there is a jump in Fe concentration on crossing the δ_{1p}–δ_{1k} boundary [20, 21]. X-ray diffraction studies, however, have not demonstrated differences between the two δ_1 layers [22], and it was hoped that Mössbauer spectroscopy may be able to shed some light on the controversy. The spectra of the two layers, though, are quite similar in that a broadened asymmetric doublet is observed (Fig. 2). Only marginal differences are noted in the values of the line splitting and isomer shift (Table I). Analysis shows the intensities of the two lines of the δ_{1p} spectrum to be similar, whereas in the δ_{1k} case, the intensity of the peak at the higher channel number (velocity) is smaller than the other because of a narrower half-width (Table I). In their transmission study, Jones and Denner [9] also observed a doublet spectrum for a synthetic δ_1 phase, which they noted could raise from the presence of two distinct Fe sites, the effect of an electric field gradient on a single site, or result from two different peaks exhibited by the δ_{1p} and δ_{1k} layers. The last possibility is ruled out by the present results.

3.3. Capital gamma, Γ, phase

The Γ phase has a homogeneity range between 24 and 31 at % Fe, and in the past has been denoted by a variety of "formulae", e.g., $FeZn_3$, Fe_5Zn_{21}, and the more accepted Fe_3Zn_{10} [11–13]. Two recent studies have brought refinements to this γ-brass-type structure. Johansson *et al.* [23] in X-ray and neutron diffraction studies on a 29.5 at % Fe alloy (approximating the formula Fe_8Zn_{18}) consider the Γ phase to be body-centred cubic with the suggestion that the inner tetrahedral sites are exclusively occupied by Fe and 35% to 70% of the octahedral sites are occupied by Fe over the homogeneity range between 24 and 31 at % Fe. Brandon *et al.* [24] from X-ray diffraction on a 24 at % Fe alloy ($Fe_{12.5}Zn_{39.5}$) find quite a different site occupancy; 4 Fe and 4 Zn in the inner tetrahedral sites and exclusively Fe in the outer tetrahedral sites. These authors suggest that the differences between their results and those of Johansson *et al.* [23] are real and reflect the different compositions of the samples examined; the sample of Brandon *et al.* [24] contained 12 Fe atoms whereas that of Johansson *et al.* [23] contained 16 Fe atoms per 52-atom cell. Thus, the structure of the Γ phase is complex with two different site occupancies proposed for samples at extreme ends of the homogeneity range. A further complication arises in considering the structure of the gamma layer due to the fact that the layer is, in fact, duplex in nature (Fig. 1c). In a recent study by Bastin *et al.* [25], using diffusion couple techniques, a new Γ_1 layer containing 18.5 to 23.5 at % Fe was observed between the Γ and δ_1 layers.

From the above it is evident that difficulties are presented in attempting to interpret Mössbauer spectra of the gamma layer. In the present work, the additional Γ_1 layer is not considered to be a problem as most of the electron back-scattered signal originates from a layer ~ 5000 Å thick [7]. Thus, the spectrum in Fig. 2 is a representation of the Γ layer with an increased contribution to the signal originating from the Fe-rich end of the phase. Analysis of the spectrum indicates that the half-width of the two peaks of the doublet are not too different (Table I) but their intensities are; the peak at the lower channel number (velocity) has an intensity about 1/4 of that of the other peak. Somewhat similar doublet spectra have been reported in the Mössbauer transmission study of Jones and Denner [9] on a synthetic Γ phase, and more recently by Montreuil and Evans [26] on a powder metallurgical Γ phase alloy with 23 at % Fe. The present peak intensity ratio of 1/4 is somewhat lower than would be anticipated from the structural study of Johansson *et al.* [23]. In view of the complex nature of the gamma layer further experiments are suggested to facilitate interpretation of the spectra in terms of particular site distributions of Fe. For example, thicker Γ (and Γ_1 layers) could be prepared by high-temperature annealing [25], and depth-selective electron back-scattering Mössbauer spectroscopy [27] performed on both sides of each layer to study the changes in spectra which may occur with layer composition in an attempt to relate the spectral intensities to the site occupancies of Fe proposed by Johansson *et al.* [23] and Brandon *et al.* [24].

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