

## Quantitative Determination of Phase Fractions in Galvannealed Steels Using XRD spectrum

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### ABSTRACT

Quantitative method of phase fraction of iron-zinc intermetallic phases formed in galvannealed steels was proposed. Pure phase spectrum could be extracted from the mixture of XRD spectrum without any pure standard reference samples which is practically difficult to prepare. A procedure for estimating phase fractions was also proposed, which is based on the regression model subject to the non-negativity constraint on coefficients. The performance of the proposed approach was verified by predicting the concentration of the mixture of powder materials with known fraction.

KEY WORDS : Galvannealed steel, phase fraction, X-ray diffraction spectrum

### 1. Introduction

Galvannealed steel sheets have been used for automobiles because they have excellent corrosion resistance, paintability and weldability.<sup>1</sup> They are produced by annealing hot dip galvannealed (zinc coated) steel, in which iron and zinc are interdiffused to form iron-zinc alloys. Within these alloy coatings, several iron-zinc phases such as Zeta, Delta and Gamma may be present. Delta phase had good friction characteristics during the press forming operation, while Gamma phase increased the powdering phenomenon which is the internal failure within coating caused by compression deformation in stamping or bending. It is known that the presence of Eta phase (Zn) has an unfavorable effect on weldability and paintability.

Since the manufacturer of most suitable

coatings requires the identification of phases, the quantitative determination of phase fractions present in galvannealed steel is necessary. There are some qualitative and semi-quantitative methods for the phase analysis of galvannealed coatings.<sup>2</sup> They may utilize some image analysis techniques that can be applied to the surface and/or cross sectional image, but this is not easy because different phases may not be clearly seen or divided.

X-ray diffraction (XRD) is widely used for the analysis of phases formed in galvannealed steel. The presence of a particular phase can be identified by its peak in the XRD spectrum. The determination of each phase's fraction, however, is a difficult task. The existing quantitative method usually employs the integration of spectrum intensity around the peak of interest. It is not quite accurate for galvannealed coatings, however, since the intensity may not fit to known standard profile. Therefore, a more elaborate quantitative analysis is required for the accurate estimation of phase fractions.

In this paper, the extraction method of pure

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XRD spectrum of each intermetallic phases in a galvanized steel sheet has been proposed. We also propose a procedure for estimating the fractions of the present phases in a coating, by using the regression model with non-negative constraints on coefficients. A mixture of powder samples with known concentration were also prepared and analyzed to validate the proposed method.

## 2. Quantification Algorithm

### 2.1. The Extraction of Pure Spectrum

Independent component analysis (ICA) is one of the pure source separation methods for linearly transforming observed high-dimensional multivariate data into several statistically independent components. ICA has gained widespread attention in a variety of fields including signal processing and spectrum applications.<sup>3,4</sup>

Many researchers have tried to demonstrate the possibility of applying ICA to feature extractions for pattern recognition or data compression and these are still important research topics. In particular, ICA has been successfully applied to the study of natural scenes,<sup>5</sup> for the study of the brain in the neurosciences,<sup>6,7</sup> for face recognition<sup>8</sup> and for general object recognition and classification.<sup>9</sup> These papers have demonstrated that ICA is well suited for feature extraction, since the coefficients from ICA maintain the most important information of the original representation.

Suppose that there is a sample of  $m$  mixtures, each of which is composed of one or more pure components with the possibility of a different fraction. The total number of pure components is denoted by  $p$  ( $p \geq m$ ). Also, assume that each mixture can be observed in terms of  $n$  variables. For the above cocktail party example,  $m$  is the number of microphones for recording,  $p$  is the number of speakers in the room and  $n$  is the number of wavelengths to be recorded by a

microphone.

Let  $S_j$  be the  $j$ -th pure component which is a random variable. Then, we may assume that the  $i$ -th mixture can be represented by

$$X_i = a_{i1}S_1 + a_{i2}S_2 + \dots + a_{ip}S_p = \sum_{j=1}^p a_{ij}S_j \quad (1)$$

$(i = 1, \dots, m)$

where  $a_{ij}$  is the mixing coefficient or fraction of the  $j$ -th pure component in the  $i$ -th mixture. Let  $X_{ik}$  and  $S_{jk}$  be the  $k$ -th observed variable of the  $i$ -th mixture and the  $j$ -th pure component, respectively. Also, let  $X = (X_{ik})$  and  $S = (S_{jk})$ . Then, (1) can be rewritten as

$$X = AS \quad (2)$$

where  $A = (a_{ij})$  is an  $(m \times p)$  matrix of the mixing coefficients. The goal of ICA is to separate  $A$  and  $S$  from the observed matrix  $X$  under the assumption that  $S_j$  should be statistically independent.

From (1) we may express a single pure component  $S$  (without subscript for the simplicity of the notation) by

$$S = w_1X_1 + \dots + w_mX_m = w^T x \quad (3)$$

where  $w^T = (w_1, \dots, w_m)$  is a weight vector and  $X^T = (X_1, \dots, X_m)$  is a vector of mixtures. Then, we need to find  $w$  to extract an independent component  $S$ .

In order to maintain independence, ICA maximizes the non-Gaussianity of  $w^T x$  and ICA employs the negentropy as a non-Gaussianity measure. In general, the entropy of a random variable vector  $y$ , with a probability density function of  $f(y)$ , is defined by

$$H(y) = -\int f(y) \log f(y) dy \quad (4)$$

From the fact that the entropy is maximized when  $y$  follows a multivariate normal distribution, the negentropy  $J$  is defined by

$$J(y) = H(y_{gauss}) - H(y) \quad (5)$$

where  $y_{gauss}$  is a vector of normal random variables with the same variance-covariance matrix as  $y$ . So, the above negentropy is zero when  $y$  follows a multivariate normal distribution and it will be positive for other distributions.

The negentropy in (5) can be approximated by

$$J(y) = \{E[G(y)] - E[G(z)]\}^2 \quad (6)$$

where  $z$  is a vector of independent random variables with the standard normal distributions and  $G$  is an arbitrary non-quadratic function, such as

$$G_1(u) = \frac{1}{a_1} \log \cosh(a_1 u) \quad (7a)$$

$$G_2(u) = -\exp(-u^2/2) \quad (7b)$$

The function in (7a) is frequently used, where the constant is chosen as  $1/a_1 = 2$ .

## 2.2. The Estimation of Mixing Coefficients

Once weight vectors are determined, pure components are obtained by (3) and then, the mixing coefficients  $a_{ij}$  can be estimated by (1). This approach, however, may result in negative values, which is not valid for mixing coefficients, as in our study. The percent fraction of a pure component in a mixture should not be negative.

Hence, we suggest using the non-negative least squares method to obtain the mixing coefficients. This approach fits the following regression model for the  $i$ -th mixture (in a sample or a new mixture)

$$X_{ik} = \sum_{j=1}^p a_{ij} S_{jk} + \varepsilon_{ik}, \quad k = 1, \Lambda, n \quad (8)$$

subject to the constraints of  $a_{ij} \geq 0$  and  $\sum_j a_{ij} = 1$ , where  $\varepsilon_{ik}$  are the random error terms. To implement this we may use the Matlab

function 'LSQNONNEG (Linear least squares with nonnegativity constraints)' based on the algorithm in Lawson and Hanson<sup>10</sup>. Figure 1 shows the whole procedure for estimating the mixing fraction.

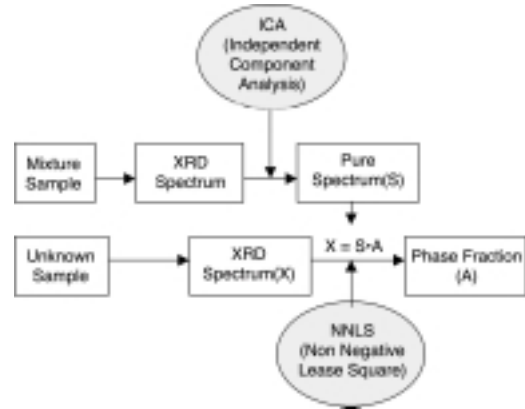


Fig. 1 The procedure for obtaining phase fraction

## 3. Application to the XRD Spectrum of Galvannealed Steels

We are interested in extracting the pure XRD spectrum of each phase present on the coatings of a galvannealed steel sheet and in estimating phase fractions by using the proposed approach. Figure 2 shows the surface layer image, from which the existence of a phase can be observed. We may also utilize some image analysis techniques based on the image in Figure 2, in order to determine the phase fractions. This is not an easy task, however, because different phases may not be clearly divided. The X-ray intensity at various angles will be observed in a form of the spectrum and used for the analysis. The presence of a particular phase can be identified by its peak in the spectrum. There have been no methods available to determine the phase fractions from this type of the spectrum.

We will apply ICA to identify the presence of a particular phase and to estimate the percent fraction of the present phase, by using the

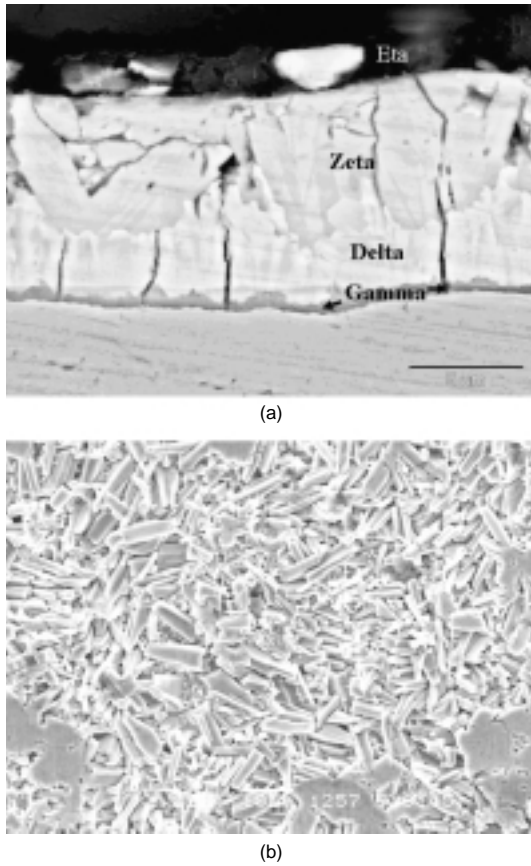


Fig. 2 Cross sectional (a) and Surface (b) image of galvanized steel

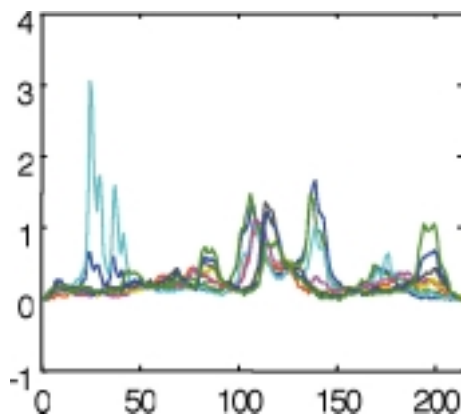


Fig. 3 The XRD spectra of galvanized steel.

proposed approach, as stated in Section 2. Figure 3 shows the XRD spectra of the 9 mixture specimens used in this study. The XRD spectra were obtained from galvanized samples using the Bruker D4 system. Cu K radiation was used as primary radiation and a Vantec detector was employed. (Bruker and Vantec are trademarks of Bruker AXS GmbH, Germany.) The intensity values are measured between 68 degrees and 78.8 in increments of 0.05, which results in 216 observed variables for each mixture.

We found, from independent component analysis, that the mixtures are composed of four phases, that is, Delta, Zeta, Eta, and Gamma, as shown in Figure 4. The pure spectrum extracted can be easily identified from the reference of Bastin *et al.*<sup>11</sup> These results can be obtained quite consistently even when a different set of mixtures is tested. In Figure 5, several XRD spectra with corresponding pure spectra are shown.

Table 1 shows the estimated phase fraction for several galvanized steels calculated by using the NNLS algorithm. The Eta phase is present when the annealing is insufficient. The shape of the pure spectrum obtained from ICA, as in Figure 4, is exactly identical to that of the spectrum from under-annealed samples. Also, we can confirm that the shape of pure the Gamma spectrum in Figure 4, is the same as that obtained from the over-alloyed samples. However, there are no samples available which contain for Delta or Zeta phases only. It seems

Table 1. The Estimated Fraction of Each Phase

Sample	Delta	Zeta	Gamma	Eta
1	41.27	48.57	0	10.16
2	55.64	44.36	0	0
3	93.83	0	6.17	0
4	25.48	18.14	0	56.39
5	97.08	0	2.92	0
6	92.30	0	7.70	0
7	83.91	0	16.09	0
8	63.30	0	36.70	0
9	39.44	0	60.56	0

consistent, however, if we compare the process parameters with the calculated Zeta and Delta fractions. As the annealing temperature and time increase, the Zeta phase transforms into the Delta phase. The Delta phase fraction, from the samples in Table 1, linearly increases with an increase in the annealing time and/or annealing temperature. From these results, we can conclude that the estimated phase fractions in Table 1 seem reasonable.

#### 4. Verification by mixing powder samples

In order to validate the proposed approach, calculation was performed using the mixture of known concentration samples.  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{MgO}$  powder type ingredients were mixed from randomly selected concentrations result to 6 samples. XRD measurements were performed from those samples using the same measurement conditions as described in the previous section. From the XRD spectra set of 6 samples, pure spectra has been calculated using ICA algorithm.

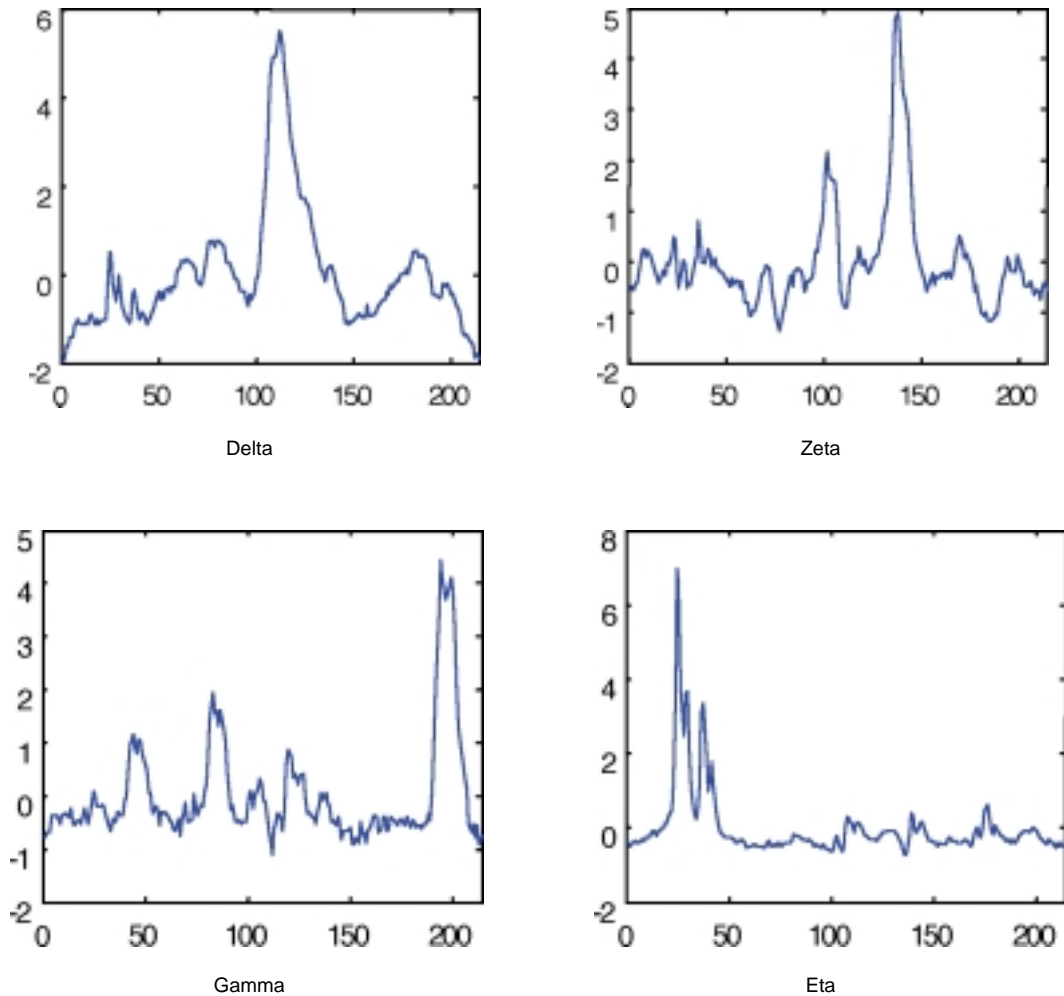


Fig. 4 Four extracted pure phase XRD spectrum

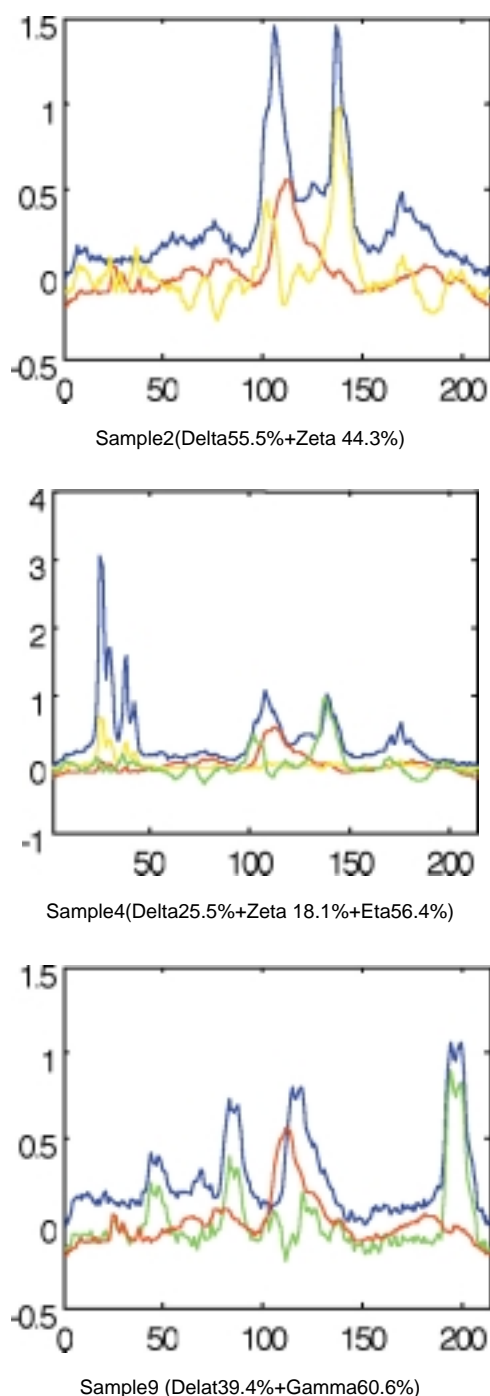


Fig. 5 Selected 3 different samples with corresponding pure phase spectrum

Concentration was estimated by NNLS approach.

Figure 6 shows original XRD spectrum for the ingredients of SiO<sub>2</sub>, TiO<sub>2</sub> and MgO. The pure spectrum extracted from the mixture of 6 samples by ICA algorithm were also shown for comparison. It is easily recognized that the extracted pure spectrum matched to the original ingredient spectrum except minor distortion at some overlapped peak position.

Table 2 shows the nominal and calculated concentration for every mixture. The mean absolute error is found to 3.79%, which is relatively small compared to commonly used curve fitting method.

Table 2 Nominal and calculated concentration of the samples.

	Nominal Concentration(%)			Calculated Concentration(%)		
	SiO <sub>2</sub>	TiO <sub>2</sub>	MgO	SiO <sub>2</sub>	TiO <sub>2</sub>	MgO
1	26.7	35.9	43.4	23.2	40.6	36.2
2	67.8	24.5	10.4	50.6	33.9	15.5
3	46.9	49.9	3.0	46.1	46.3	7.6
4	40.9	42.2	16.4	40.6	40.6	18.7
5	15.9	40.7	38.9	15.0	42.6	42.3
6	41.7	21.7	36.1	42.2	23.6	34.3

## 5. Conclusions

In this paper, the quantification method of galvanized coatings has been proposed using XRD spectrum data taken from the coatings. ICA is utilized used for separating pure spectrum from a set of mixtures of XRD spectrum, since the single phase coating is not available practically. This paper also proposed a regression-based approach by using non-negative least squares to estimate the fraction of each independent component and it is applied to the case of galvanized steel sheets.

It is confirmed, from the validation experiments, that the proposed approach works quite well within an acceptable error range. It was also observed that our approach is stable and

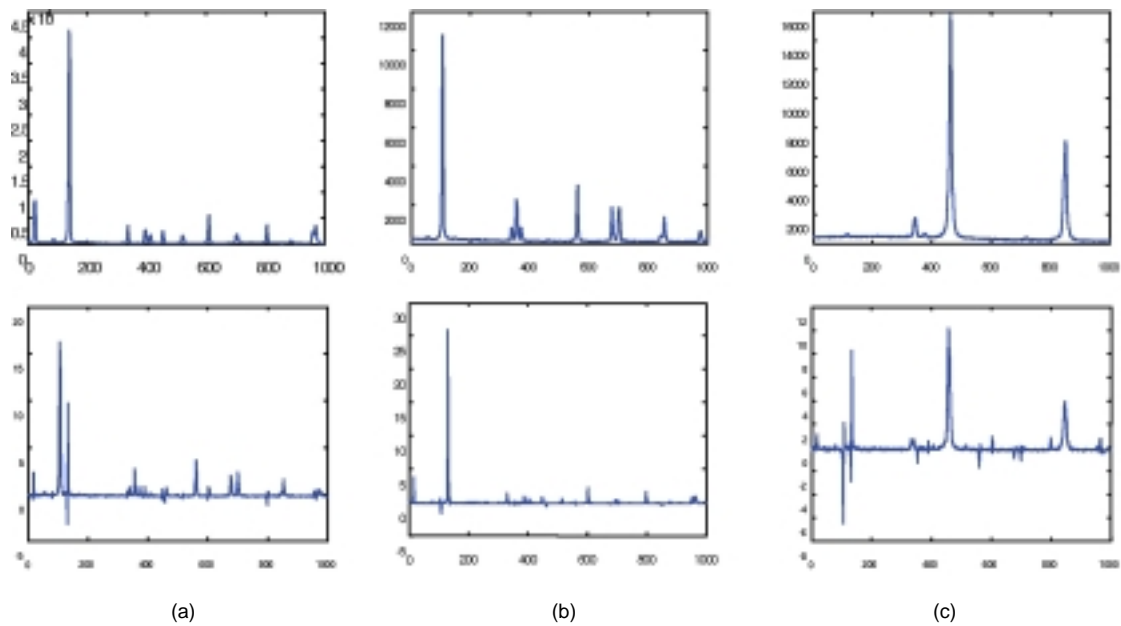


Fig. 6 Original XRD spectrum(upper) of (a)  $\text{SiO}_2$  (b)  $\text{TiO}_2$  (c)  $\text{MgO}$  and their corresponding pure spectrum(below) derived from ICA

robust to the noise level.

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