Topical Report

Chemical Analysis of XPS (X-ray Photoelectron Spectroscopy) Data using Self - Organising Maps

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Abstract

This paper reports on the application of SOM to chemical analysis of FeNi alloys from XPS (X-ray Photoelectron Spectroscopy). During the course of the experiment (XPS), either by human error or mechanical error, the conditions for the experiment does not remain the same. Thus results obtained may be slightly different from the expected. Since the composition of Fe and Ni in the alloys are varied proportionally, the XPS signals from Fe2p can be used to minimise the error margin of the XPS signals from Ni2p and vice versa, depending on the most sensitive of the two.

1. Introduction

Self-Organising Map (SOM) method developed by T. Kohonen [1] was first applied to information processing. One characteristic of the SOM is its ability to make multidimensional data visible on a 2 dimensional map. SOM can be considered as a grid with predefined but originally empty nodes. During learning, the pattern of filling of the nodes is determined by the degree of similarity between the data. Thus it is possible to distinguish between similar and dissimilar data on a 2 dimensional SOM. The magnitude of the distance between the nodes is shown by a grey level expression. The method provides an approach to data correction whiles pre-processing the input data and also to determine the alloy composition from the spectral data.

2. The SOM Algorithm

T. Kohonen [1] developed an equation, which governs the information content of a unit in the grid based on the information processing ability of the brain.

$$\boldsymbol{m}_i(t+1) = \boldsymbol{m}_i(t) + \alpha(t)[\boldsymbol{x}(t) - \boldsymbol{m}_i(t)] \qquad (1)$$

where $\boldsymbol{m}_i(t)$ is the information processing ability of the neuron cell (node) $\boldsymbol{i}$ at time t and $\boldsymbol{x}(t)$ is the input signal. At time t, the cell learns this input signal. During time $(t+1)$, the information processing ability of the cell becomes $\boldsymbol{m}_i(t+1)$. If $\boldsymbol{x}(t)$ is an n-dimensional input vector, then $\boldsymbol{x}(t) = [\xi_1, \xi_2, \ldots, \xi_n]$ and the n-dimensional reference vector $\boldsymbol{m}_i(t) = [\mu_{i1}, \mu_{i2}, \ldots, \mu_{in}]$. $\alpha(t)$ is the learning coefficient factor with values between 0 and 1. When an n-dimensional input vector is introduced to the network, the reference vector in the network (node) that is closest to the input vector is defined as the best-matching node "winner" and its information processing ability is denoted by $\boldsymbol{m}_c(t)$. Prior to learning, a large reference area surrounding the winner is selected as a neighbourhood region. The reference unit vectors in this neighbourhood region $N_c(t)$ as well as the winner $\boldsymbol{m}_c(t)$ learn the input vector $\boldsymbol{x}(t)$ following eq.1. This forms a typical learning cycle. The next cycle begins with the introduction of the next input vector but with a reduced neighbourhood region. Learning continues until only the winner is trained. Furthermore, $\alpha(t)$ reduces to 0 as learning progresses. For the case of this experiment, $\alpha(t)$ is a linear decreasing function.

$$\alpha(t) = \alpha_0(1 - t/T), \qquad (2)$$

α_0 is the initial value, t is the present learning cycle and T is the maximum number of the learning cycles after which learning is terminated. Other types of decay functions for α can be considered.

3. Data Pre-processing and Correction

It is advisable that the input data be normalised prior to its introduction to the network. This is to ensure that the differences among the data are maximised. The numerical accuracy of statistical computations in connection with the SOM algorithm improves considerable when the input data is normalised [1]. The XPS signals from Ni2p are used to correct the error in the XPS signals from Fe2p. The following is the relationship between the two signals:

$$Fe_{20} \propto (Ni_{80}) \qquad (3)$$

$$Fe_{50} \propto (Ni_{50}) \qquad (4)$$

$$Fe_{70} \propto (Ni_{30}) \qquad (5)$$

$$S_x = \left(\frac{Max.\ Fe2p_x - Min.\ Fe2p_x}{Max.\ Ni2p_x - Min.\ Ni2p_x}\right)\left(\frac{x}{1-x}\right) \qquad (6)$$

$$S_{av} = \frac{S_{20} + S_{50} + S_{70}}{3} \qquad (7)$$

$$Norm.\ Fe2p_x = \frac{Fe2p_x}{Fe2p_x + S_{av}(Ni2p_{(1-x)})} \qquad (8)$$

where x is the percentage composition of the alloy and S_x is the proportionality constant between XPS signals from Fe2p and Ni2p.

4. Chemical Data Mining Analysis

Binding energies of XPS data from 700eV to 735eV in increments of 0.05eV are considered as dimensional units. Each spectrum is a 530 dimensional input vector.

The signal value of the spectrum are then normalised as in section 3 and used as input vector for the SOM [2]. 5 samples of FeNi alloy (Fe100Ni0, Fe80Ni20, Fe50Ni50, Fe30Ni70 and Fe0Ni100) spectra shown in Fig. 1 are used as input data.

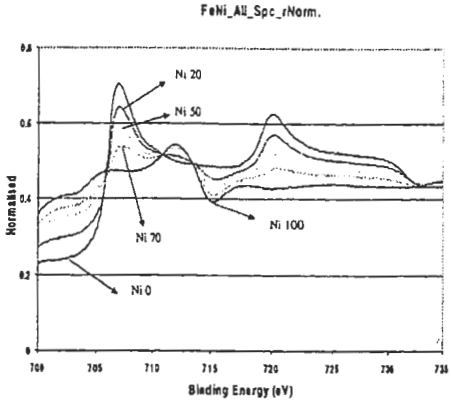

Fig. 1 Normalised data using both Fe2p and Ni2p results.

For the purposes of data mining, the dimensional values of Fe30Ni70 are excluded from the input data. The compositions of the alloys are also considered as new dimensional units with values between 0 and 1. For instance Fe80Ni20 alloy has 20% nickel and is therefore denoted by 0.2. SOM is constructed from the multidimensional data of Fig. 1 into a 2 dimensional 20X30-neuron unit using grey level expression in Fig. 2

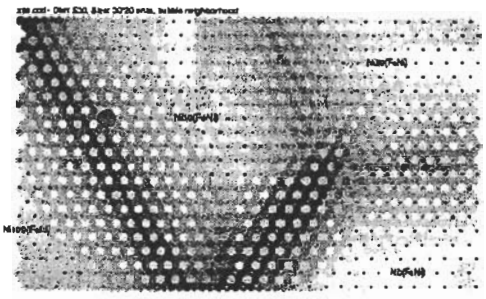

Fig.2 SOM of XPS on 20X30 unit grid. The large filled circle is the best match unit for Fe30Ni70 alloy.

After SOM learning, all the 600 units or nodes on the grid are compared by the Error function Err:

$$Err = \sum_{j=1}^{n} (x_j - m_{ij})^2, \qquad (3)$$

where x_j and m_{ij} are the j-th component of the n-th dimensional input data and the i-th unit (node) respectively. The labelled positions of the 20X30-unit grey scale map are determined by the minimum value of the Error function.

Fe30Ni70 alloy was excluded from the input data and is now used as test data to test the generalising ability of the network. By use of eq. 3, all the 600 nodes or units of Fig. 2 are compared with the test data of Fe30Ni70 alloy. The unit with minimum value of the Error function is identified as the best match unit. For this experiment, the closest unit was identified as Fe29.9Ni70.1as shown in Fig. 3 with a composition error of 0.1%. Table 1 shows the data mining simulation results for various compositions from two different labs.

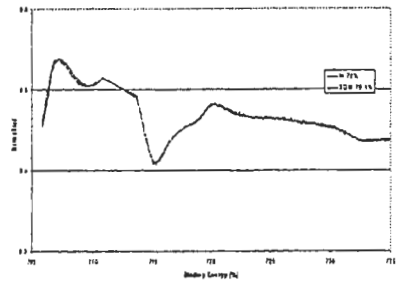

Fig. 3. XPS spectra of the original Fe30Ni70 input data and the learned best match spectra. Learning cycles 1000.

Lab	$Fe_xNi_{(1-x)}$ Alloy	Composition Error (%)	Mean Squared Error (%)
XPS	Fe30Ni70	0.5	0.004
Lab. A	Fe50Ni50	1.5	0.006
Exp. 1	Fe80Ni20	5.0	0.008
XPS	Fe30Ni70	0.1	0.003
Lab. A	Fe50Ni50	0.4	0.002
Exp.2	Fe80Ni20	4.4	0.006
XPS	Fe30Ni70	3.0	0.10
Lab. B	Fe50Ni50	18.7	1.22
	Fe80Ni20	1.0	0.05

Table. 1 Simulation results of data from 2 different labs. with varying degree of data error.

5. Conclusion

This paper reports on the application of SOM to chemical analysis of FeNi alloys from XPS data performed under varying conditions as a result of either human error or mechanical error. Thus results show that the level of spectral distortion as a result of mechanical or human error affects the numerical accuracy of the statistical computation. For effective cluster classification, the input data though independent must be somewhat related. Experimental or human errors that cause higher distortions in the spectral shapes of the data result in high composition error and mean squared error even after the data is corrected. From the results obtained in the experiment, it is obvious that the SOM is a good tool for data mining. The composition of unlabeled spectra can be determined from the spectral data learned by the SOM.

Furthermore, if a labelled spectrum with incomplete characteristics or dimensions is placed on the grid, the missing characteristics or dimensions can be derived from the data that has already been assigned to the empty grid through the learning process.

References

[1] T. Kohonen, Self-Organising Maps, Springer Series in Information Sciences, Vol.30, 1995.

[2] H. Tokutaka, Application of Self Organising Map to Chemical Analysis. Proceedings of ICONIP'97, pp. 1318-1321 (1997)