Wavelet transform electrochemical noise analysis for intermetallic coatings at 750 °C in molten salt environment.

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Summary

Localized corrosion at high temperature is the most dangerous form of corrosion, which often causes unexpected and rapid damage to a very small portion of a metal structure. Electrochemical noise (EN) measurement can provide information about both the rate and the mechanism of a corrosion process. The intensity of the corrosion process is associated to the amplitude of the fluctuations observed in electrochemical noise measurements (ENMs) and their shape related with the type of corrosion process. Most ENRs are characterized by a high number of overlapped transients. Hence, the signal analysis requires adequate mathematical tools. The wavelet analysis is a mathematical tool for data processing and has been proposed since 90 decade as an alternative to Fourier transform when a precise time-scale analysis is required or to study transients into a signal. The aim of this work is to show that wavelet analysis can be a valuable option to process ENMs data obtained from high temperature intermetallic coating corrosion

1 Introduction

Intermetallic compounds have emerged as materials with vast potential for application in a wide range of technologically areas [2]. The relevance of intermetallics stems from their many attractive properties, such as high oxidation and corrosion resistance and relatively low densities, combined with their ability to retain strength and stiffness at elevated temperatures [3, 4]. Many investigations in intermetallics has been done principally in the Ni–Al system [5], however, this system is not yet available for structural applications. Intermetallic compound in Ni-Al systems, together with γ'-Ni_3Al, has been used as a coating material for Ni-base superalloys, because of its excellent oxidation resistance conditions. In the energy production industry, the fuel oil combustion play a key role over boiler materials performance. High air excess during the combustion process enhances high temperature oxidation of super-heaters and re-heaters, accelerated by vanadium and sulfur compounds. This condition also increases the generation of SO_3 and hence the corrosion by sulfuric acid in the low temperature zone of the boiler [6]. Here intermetallic NiAlCu type materials was thought to be successful in order to withstand the high temperature corrosion as a coating for Ni base superalloys applied by HVOF deposition technique.

On the other hand electrochemical noise measurements (ENMs) provide information of corrosion mechanisms, so this technique was eligible to monitor the NiAlCu coating hot corrosion process. The amplitude of the fluctuations observed in electrochemical noise records (ENRs) can be correlated with the intensity of the corrosion process, while the fluctuation shape observed in these records can be correlated with the type of corrosion process [7]. According to A. Aballe et al. electrochemical noise analysis often requires appropriate mathematical tools. Statistical methods have been proposed, based on spectral and other chaos theory. Bertocci et al. [8, 9] suggested that due to the inhomogeneity of the test electrodes during the ENMs it was possibly to cause a low frequency trend or DC trend coupled in the potential or current fluctuation which will produce $1/f^2$ slopes in the PSD plots. Mansfeld et al. [10] says that the standard deviation of fluctuations in the potential and current V and σV and σI could change, affecting directly the values of noise resistance, which is given by the relationship Rn= σV/σI [11, 12, 13]. Y. J. Tan et al. [14] used a method of removal of the trend called MAR. The thought behind this is to remove the method average noise values from the record. Recently a mathematical tool developed several years ago called discrete wavelet transform (DWT) was applied for this purpose. Since one of the disadvantages of statistical methods is that they analyze signals by averaging the features across the whole time record, the discrete wavelet transform (DWT) has been proposed as a method of analysis that meets the aforementioned limitations under hot corrosion phenomena.

2 Experimental Procedure and DWT analysis

The coating process of the NiAlCu intermetallic over the Ni superalloy substrate was detailed elsewhere [15, 16]. NiAlCu coating samples were cut to obtain 10x10mm flat squares surfaces with 1 mm thickness. Each sample was welded on one of its sides to nicromel wire (80Cr-20Ni). Once welded samples were placed inside a ceramic tube with dimensions of 8.09 mm OD, 5.00mm inner diameter and 200mm in length and the tube is sealed by the part of the sample with refractory cement. This device (electrochemical cell) was then installed in a vertical electric furnace, once the corrosive salt mixture is introduced was contained in a 20ml ceramic crucible inside the vertical furnace, which was maintained at a temperature of 750°C ± 4°C during the test period. The temperature inside the furnace was monitored by a K type thermocouple, which in turn is connected to an analog meter.

ENMs were carried out, using a Gill AC from ACM Instruments, controlled by a desk top computer. Two nominally identical electrodes were used attached to the Gill AC equipment and taking readings in blocks of 1024 points taken at 1 s interval. The wavelet analysis was carried out by matlab 7.8 software.

3 Results and Discussion

After 12h of immersion of the NiAl-Cu intermetallic HVOF protective coating in the molten salts at 750°C, typical potential and current fluctuations are shown in Fig. 1. The current noise (i) transients well as potential (E) noise transients present repetition frequencies with amplitudes of $12X10^{-5}$µA and 20mV respectively. As can be seen both the potential and the current fluctuations are very regular and occur in phase with each other, that is, their fluctuations always occur simultaneously. However, there are many other transients generated due the beginning of metastable pits.

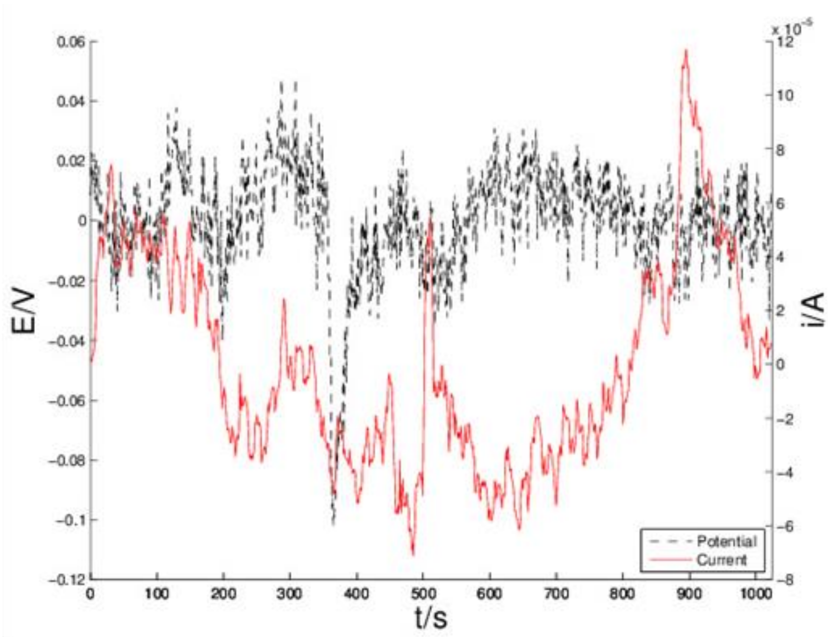

Figure 1: Electrochemical Noise Measurements (ENMs) Transients

The spectral noise resistance R_{sn} *(f)* introduced by Mansfeld et al. [13] was calculated from the measured data shown in Fig. 1. This is plotted in Fig. 2 (without mean removal).

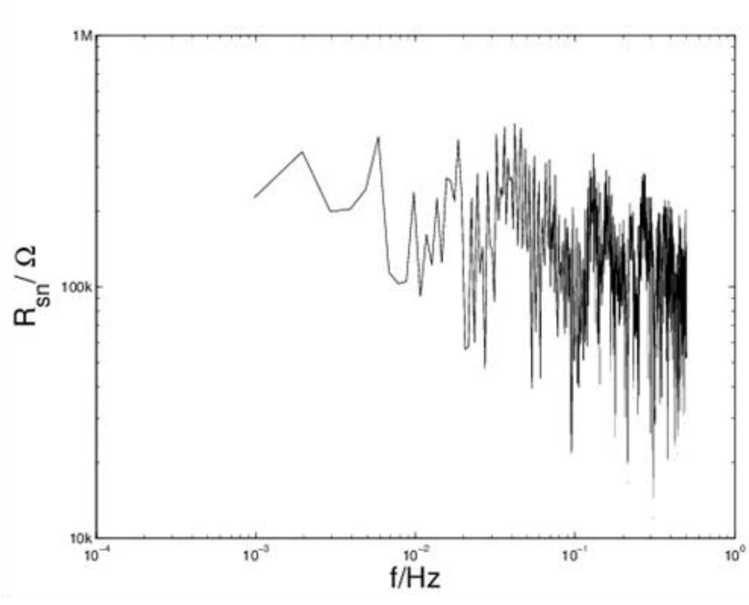

Figure 2: Spectral Noise Resistance

The first step of the proposed wavelet analysis method consists of estimating DWT for each time series whose mean has been previously removed. The boundary conditions imposed to perform DWT in this paper are those that consider that wavelet are zero outside the range of the time record [7, 12, 13]. This condition limits the type of wavelet that can be selected to the symmlets wavelets [10].

A way of representing the results of DWT is estimating the contribution of each coefficients decomposition to the overall signal. The overall power of signal or energy is calculated with the aid of the following equations [17-19]:

$$E=\sum_{n=1}^{N} x_n^2 \qquad n=1,...,N \qquad (1)$$

The fraction of energy associated with each j detail coefficient decomposition is calculated as follows,

$$E_j^d=\frac{1}{E}\sum_{n=1}^{N/2^j} d_{j,n}^2 \qquad j=1,\ldots,J \qquad (2)$$

for smooth coefficient at level J the equation is similar,

$$E_J^s=\frac{1}{E}\sum_{n=1}^{N/2^j} s_{J,n}^2 \qquad (3)$$

Because the symmlet wavelets are orthogonal, the following equation is satisfied:

$$\sum_{n=1}^{N} x_n^2=\sum_{j=1}^{J}\sum_{n=1}^{N/2^j} d_{j,n}^2+\sum_{n=1}^{N/2^j} s_{J,n}^2 \qquad (4)$$

In Fig. 3 we plot the relative energy accumulated $E^d{}_j$ or $E^s{}_J$ by each level decomposition versus j until level *J=7*. This kind of plots are called energy distribution plot (EDP). The high value for *d=7* in both current and potential reflect the fact that transients with a large scale prevail over those with small scale in the original signal. Moreover the high value for *s=7* tell us that the intensity of the trend is bigger than the intensity of the transients in both signal, but more pronounced in the current signal.

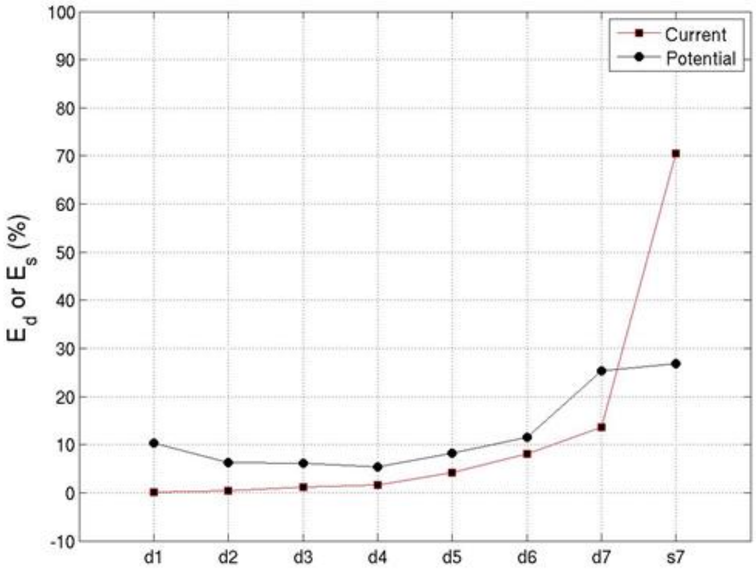

Figure 3: EDP corresponding to the ENMs in Fig. 1.

Now we want to analyze the results of DWT in relation with the noise resistance quantity R_{sn}, for this purpose we can use the definition of noise resistance based on DWT given by the following equation [9]:

$$R_n(J) = \frac{\sigma(H_{V,J})}{\sigma(H_{C,J})} \quad \textbf{(5)}$$

where $H_{V,J}$ and $H_{C,J}$ represent the sum of all detail coefficients of the potential and current noise below level J, respectively, σ represents the standard deviation. In Fig. 4 is showed the plot of noise resistance Rn (J) for each accumulated level J. It can be seen that Rn (J) decrease monotonically with the increasing J until reach its minimum value at Rn which is the noise resistance of the overall signal x(t).

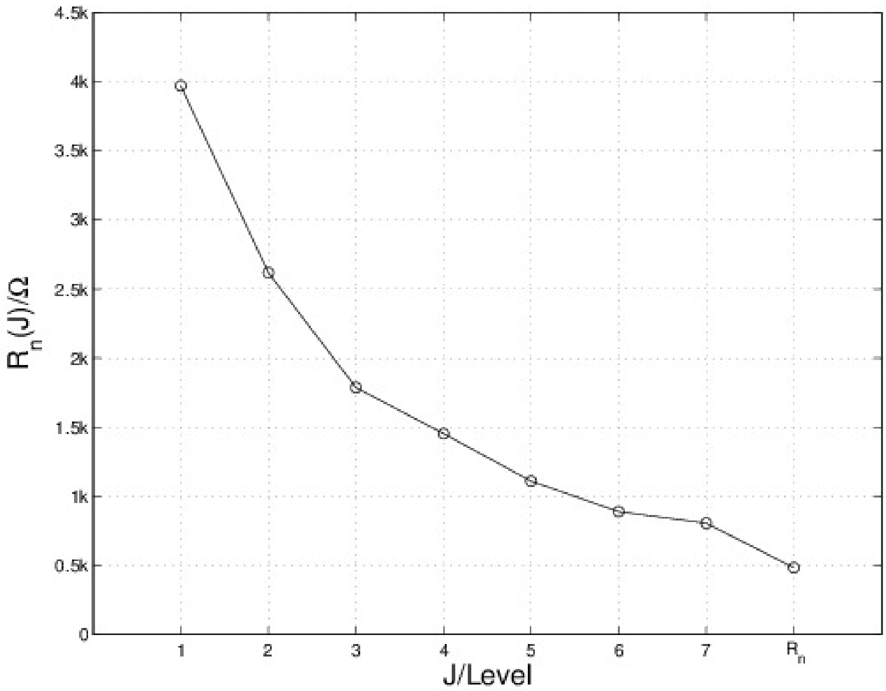

Figure 4: Level accumulated of the noise resistance corresponding to the ENMs in Fig. 1

4 Conclusions

The wavelet transform is a tool that cuts up data or functions or operators into different frequency components, and then studies each component with a resolution matched to its scale. The wavelet transform of a signal involving in time depends on two variables: scale (or frequency) and time; wavelets provide a tool for time-frequency localization. In this paper wavelet transform has been used to the study of electrochemical noise retrieved from hot corrosion phenomena. A brief description of this mathematical tool has been presented. Its utility have been given to show the adequacy of wavelet transform for analyzing electrochemical noise records. In general, wavelet analysis seems more versatile for extracting the diverse components contained within one overall ENMs and to weight their relative contribution. However, more research and analysis discussion is needed to obtain more conclusive data confirming the definitive validity of this mathematical methodology technique.

5 References

[1] Ewa Beltowska-Lehman, Surface and Coatings Technology (2002), pp. 440–443.

[2] R. Darolia, J. Met. 43, 3, (1991) pp. 44–49.

[3] E. P. Busso, F. A. Mcclintock, Acta Metall. Mater. 42, (1994), pp. 3263–3275.

[4] R. Jayaram, M. K. Miller, Acta. Metall. Mater. 42, (1994), pp. 1561–1572.

[5] R. D. Field, D. F. Lahrman, R. Darolia, Acta Metall. Mater. 39, (1991), pp. 2951–2959.

[6] J. Castrejon, S. Serna, A. Wong-Moreno, A. Fragiel, D. Lopez-Lopez, Materials Science and Engineering A 415 (2006) 118–125.

[7] A. Aballe, M. Bethencourt, F.J. Botana, M. Marcos, Electrochemistry Communications 1 (1999) 266–270.

[8] U. Bertocci, J. Frydman, C. Gabrielli, F. Huet, M. Keddam, J.Electrochem. Soc. 145 (1998) 2780.

[9] Zehua Dong, Xingpeng Guo, Jiashen Zheng, Liming Xu, Electrochemistry Communications 3 (2001) 561-565.

[10] F. Mansfeld, Z. Sun, C.H. Hsu, A. Nagiub, Corrosion Science 43 (2001) 341-352.

[11] C. Cuevas-Arteaga, J. Porcayo Calderón, Materials Science and Engineering A 435-436 (2006) 439-446.

[12] M.A. Lucio-Garcia, J.G. Gonzalez-Rodriguez, M. Casales, L. Martinez, J.G. Chacon-Nava, M.A. Neri-Flores, A. Martinez-Villafañe, Corrosion Science 51 (2009) 2380-2386.

[13] F. Mansfeld, Z. Sun, Corrosion; Oct. 1999; 55, 10; ProQuest Science Journals pg. 915.

[14] Y. J. Tan, S. Bailey and B. Kinsella, Corrosion Science, Vol. 38, No. 10, (1996) pp. 1681-1695.

[15] J. Colín, S. Serna, B. Campillo, R.A. Rodríguez, J. Juárez-Islas, Journal of Alloys and Compounds, 489, 1, 2010, pp 26-29

[16] C.D. Arrieta-Gonzalez, J. Porcayo-Calderon, V.M. Salinas-Bravo, J.G. Chacon-Nava, J.G. Gonzalez-Rodriguez, International Journal of Electrochemical Science, Vol 6, No 8 (2011) 3644 –3655

[17] Daubechies, Ten Lectures on Wavelets, Society for Industrial and Applied Mathematics, Philadelphia, PA, 1992.

[18] A. Bruce, H.-Y. Gao Applied Wavelet Analysis with S-Plus, Springer, New York, 1996.

[19] A. Cohen, I. Daubechies, P. Vial, Appl. Comput. Harmonic Anal. 1 (1993) 54.