

The fractal dimension as estimator of the fractional content of metal matrix composite materials

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Abstract Electrochemical techniques are applied to estimate the fractal dimension value of electroactive surface structures. However, the fractal dimension value is an abstract concept, which sometimes is hard to understand. Herein, this abstract concept is used to calculate the fractional content of the nickel/graphite–polypropylene hybrid composite material, putting into practice this concept in the study of composite materials.

Keywords Nickel/graphite–polypropylene hybrid composite material · Fractal dimension value · Fractional content · Percentage of electroactive surface · Chronoamperometry · Cyclic voltammetry

Introduction

A metal matrix composite is a composite material with at least two constituent parts, one being a metal, such as nickel, whereas the other constituent may be a different metal or another material such as graphite. This kind of materials is called hybrid composite when at least three different materials are present. Hybrid composite materials have become increasingly important in electronic industries such as antistatic, electromagnetic, and radio frequency

interference shielding and for magnetic tapes [1–3]. Furthermore, they are widely used industrially in low density metal structures and as negative electrode materials in batteries [4]. The nickel/graphite–polypropylene hybrid composite material corresponds to the latest generation of metal matrix composite materials. This novel material is actually developed to fight electromagnetic contamination as well as to replace the metallic nickel by a material that can be mechanized easily by means of techniques employed in the plastic manufacture.

The physical properties of these composite materials are governed by the properties of the clusters that are formed when contacts are established between the reinforcement materials embedded into the polymeric matrix [5, 6]. The formation of these clusters depends on the fractional content of the composite material. When the largest cluster spans the macroscopic dimension of the sample, the system is said to percolate, and such a cluster is referred to as a percolating cluster or an ‘infinite cluster’. The larger clusters acquire a fractal character when the percolation threshold is approached [7].

Several studies [6, 8, 9] have characterized the behavior of the percolating networks and their physical properties by determining scaling ratios and fractal dimensions. Rigorous tests of theoretical models require accurate determinations of the fractal dimension value (f_d) of the surface structure. Available methods to determinate this dimension can be classified as physical, chemical, and electrochemical. The most common electrochemical methods are based on chronoamperometric and voltammetric measurements [10–12] and they characterize only the electroactive surface in a specific experimental condition [13]. The electrochemical calculus of the fractal dimension value is based on the time and potential dependence on the diffusion-limited current intensity (j), which can be describes by means of the

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Cottrell equation. Thus, the chronoamperometric method is based on [10]:

$$j(t) = \sigma_F t^{-\left(\frac{fd-1}{2}\right)} \quad (1)$$

where σ_F is the fractal Cottrell coefficient and t the time. By plotting j vs. t in a log–log diagram, one obtains fd from the slope of the linear fit.

The voltammetric method is based on the realization that the peak current intensity, j_{peak} , can be written as [11, 12]:

$$j_{\text{peak}} \propto \nu^{\left(\frac{fd-1}{2}\right)} \quad (2)$$

where ν is the scan rate. By carrying out voltammetric measurements at different scan rates, and plotting j_{peak} vs. ν in a log–log diagram, fd is obtained from the slope of the linear fit of this plot.

The main goal of this work is to calculate the fractional content of metal matrix composite materials by means of the fractal dimension value, putting into practice this abstract concept in the study of these materials. For that, electrochemical methods are here used to calculate the fractal dimension value of the electroactive surface in a specific experimental condition.

Experimental

Electrochemical measurements were carried out in a typical electrochemical three-electrode cell. A platinum plate was used as the counter electrode and an Hg|HgCl|KCl_{sat} electrode as the reference electrode. The working electrode was made from a polycrystalline nickel sheet (99.9%, Johnson & Matthey) or a nickel/graphite–polypropylene hybrid composite material (PPCNi) sheet. In the composite material, the polypropylene is the matrix material, whereas the nickel—with a mean diameter of 5 μm —and the graphite—Merck sheets with a mean diameter of 15 μm —are reinforcement materials. This composite material was prepared by means of the method previously described in [3]. The fractional content in weight is: 50% polypropylene, 40% graphite, and 10% nickel.

The electrolyte used in all experiments was 5 mM H₂SO₄ (Merck, a.g.), 0.25 M K₂SO₄ (Scharlau, a.g.), and NiSO₄ (Merck, a.g.) with pH 2.0. The cell was thermostated at 298 K by means of a HETO DENMARK bath and bubbled with Ar (Air Liquide S.A., U-N45) for about 10 min (inert atmosphere). Electrochemical experiments were performed by using a potentiostat Wenking HP88 whereas the potential and current values were recorded in a Keithley 2700 multimeter. Fractional contents and images of the working electrode surface were obtained from an environmental scanning electron microscope (XL-30 ESEM, Philips).

Results and discussion

Figure 1 shows chronoamperometric data for the anodic electrodisolution of the metallic nickel embedded into the nickel/graphite–polypropylene hybrid composite material. In this figure, zone 2 identifies the time range where the diffusion of anions in the electrolyte limits this electrodisolution process [3, 14], whereas zone 1 is characterized by a kinetic reaction control. The resistive control of the current intensity can be considered to be negligible in zone 2 and during voltammetric scans given that the resistance of this hybrid composite material is 3 Ω [3] and current intensities are small [15, 16]. Therefore, and as Eq. (1) is deduced considering a diffusion-limited current intensity, the fractal dimension value of PPCNi surface is here calculated from the logarithmic fit of the chronoamperometric data of zone 2. The coefficient of correlation of this fit corresponds to 0.99 which confirms that the current intensity is limited by diffusion in this time zone since these chronoamperometric values can be fitted by means of the Cottrell equation. Thus, and as the slope of this logarithmic fit is -0.41 , the fractal dimension value in these experimental conditions for the electroactive surface structure of the nickel/graphite–polypropylene hybrid composite material is equal to 1.82, as Eq. (1) shows.

Fractal structures with a range of $1 < fd < 2$ describes surfaces with non-electroactive zones [10] where the amount of these zones depends on the experimental conditions. This is due to the self-affinity property of fractal surfaces [17]. The self-affinity refers to a fractal object whose pieces have to be rescaled using an anisotropic transformation in order to appreciate the self-similarity. If the geometric surface was completely electroactive, then the calculus method of the

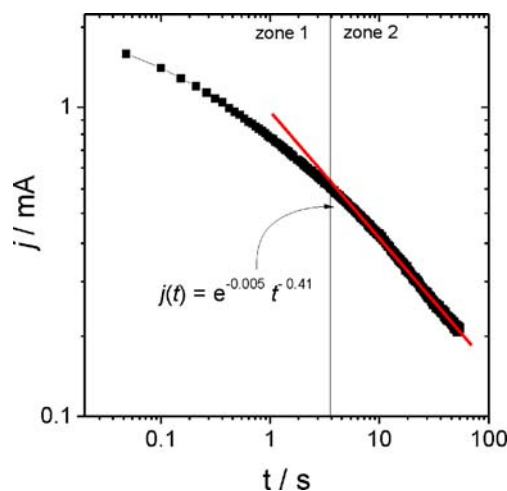


Fig. 1 Chronoamperometry of the anodic electrodisolution of the metallic nickel embedded into the nickel/graphite–polypropylene hybrid composite material. Experimental conditions were 5 mM H₂SO₄, 0.25 M K₂SO₄, and pH 2.0 at 0.08 V. The cell was thermostated at 298 K and bubbled with Ar

fractal dimension value should rescale using an isotropic transformation and, thus, the fractal dimension value should be two or greater than two.

Next, the fractal dimension value of the electroactive surface structure of the nickel/graphite–polypropylene hybrid composite material is verified by means of the voltammetric method (Eq. (2)). Figure 2 shows the evolution of the current intensity of the anodic voltammetric peak (j_{peak}) with respect to the scan rate (ν). The linear fit of this logarithmic diagram gives a slope equal to 0.41, which is an estimation of the fractal dimension value considering Eq. (2). Accordingly, the fractal dimension value of the electroactive surface of the working electrode in these experimental conditions corresponds to 1.82. The good correlation between the fractal dimension value calculated by this method and the chronoamperometric method proves that the right fractal dimension value of this electroactive surface structure in these experimental conditions is around 1.82.

Calculating the percentage of electroactive surface from the fractal dimension value, this dimension is related to the surface area, A , through the scaling law [18]:

$$A(\lambda) = A_0 \lambda^{-(fd-2)} \tag{3}$$

where λ is the scaling ratio and A_0 is the geometrical area of the working electrode.

If the surface of the working electrode is assumed smooth and therefore, the fractal dimension value is only due to percolation clusters—in general, this is like that in composite materials—then the fractal dimension value can be related to the percentage of electroactive surface in each

experimental condition, $P(\%)$, dividing Eq. (3) by the geometrical area:

$$P(\%) = \frac{A_0 \lambda^{-(fd-2)}}{A_0} = \lambda^{-(fd-2)} \tag{4}$$

Estimating the scaling ratio employed in the electrochemical calculus methods, it is necessary to calculate the fractal dimension values for two different electroactive surface structures. Thus, Fig. 3 shows the evolution of the current intensity of the anodic voltammetric peak with respect to the scan rate for a working electrode made from polycrystalline nickel. This plot has a slope equal to 0.43, which corresponds to a fractal dimension value of 1.86, as can be estimated from Eq. (2). The fractal dimension value of the polycrystalline nickel surface structure is lesser than two because the nickel is passivated in these experimental conditions (non-electroactive zones) [19–22].

Once the fractal dimension of two different electroactive surface structures is calculated, the scaling ratio can be estimated taking into account that the peak current intensity is directly proportional to the electroactive surface area of each experimental condition [23]. Thus, Eq. (3) can be converted into:

$$I_{\text{peak}}(\lambda) = I_{\text{peak}}^0 \lambda^{-(fd-2)} \tag{5}$$

where I_{peak}^0 is the peak current intensity when the electroactive surface was equal to the geometric surface. Therefore, if two different fractal structures have the same geometrical area, then:

$$\lambda = \left(\frac{I_{\text{peak}}^1}{I_{\text{peak}}^2} \right)^{\frac{-1}{(fd^1 - fd^2)}} \tag{6}$$

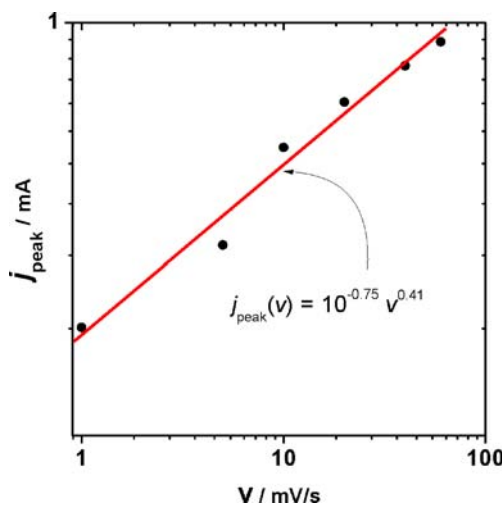


Fig. 2 Evolution of the current intensity of the anodic voltammetric peak with respect to the scan rate for the working electrode of the nickel/graphite–polypropylene hybrid composite material. Experimental conditions were 5 mM H₂SO₄, 0.25 M K₂SO₄, and pH 2.0. The cell was thermostated at 298 K and bubbled with Ar

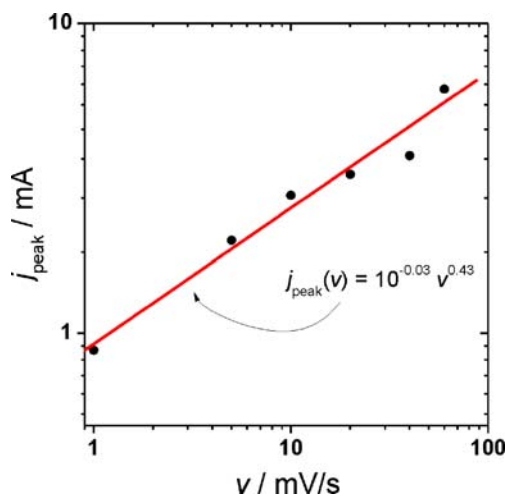


Fig. 3 Evolution of the current intensity of the anodic voltammetric peak with respect to the scan rate for the working electrode of the polycrystalline nickel. Experimental conditions were 5 mM H₂SO₄, 0.25 M K₂SO₄, and pH 2.0. The cell was thermostated at 298 K and bubbled with Ar

Considering that the studied working electrodes of polycrystalline nickel and nickel/graphite–polypropylene hybrid composite were made from the same geometrical area, the experimental results of Figs. 2 and 3 allow to estimate the scaling ratio of the electrochemical methods from the Eq. (6). This ratio is equal to $4 \cdot 10^{-8}$.

As commented above, the electroactive area is directly proportional to the peak current intensity, which is also directly proportional to the amount of electroactive species of the working electrode in each experimental condition [23]. Consequently, the percentage calculated from Eq. (4) may also correspond to the fractional content of electroactive species of this electrode:

$$P(\%) = \frac{A_{\text{electroactive}}}{A_0} \frac{I_{\text{peak}}}{I_{\text{peak}}^0} \frac{n_{\text{electroactive}}}{n_{\text{geometric_surface}}} = \lambda^{-(fd-2)} \quad (7)$$

where $n_{\text{geometric_surface}}$ are moles of particles in the geometric surface and $n_{\text{electroactive}}$ are moles of electroactive species in a specific experimental condition.

As Figs. 1 and 2 only show the electrodisolution process of the metallic nickel that compose the composite material since there is no other electroactive species in the working solution, the fractal dimension value calculated from these experiments only characterizes the percentage of the nickel electroactive surface of the composite material. From a fractal dimension value equal to 1.82, Eq. (7) estimates the fractional content of nickel into the nickel/graphite–polypropylene hybrid composite material around 5%. This result was checked by the environmental scanning electron microscope, which estimates the fractional content of nickel around 3%. The good correlation between experimental and theoretical data agrees with the use of Eq. (7) to estimate this fractional content.

The nickel/graphite–polypropylene hybrid composite material is composed of two conductor reinforcement materials, which are nickel and graphite. Calculating the fractional content of graphite, Fig. 4 shows chronoamperometric data for the electrodeposition of metallic nickel on all electroactive surface of the composite material. In these experimental conditions, the electroactive surface of this composite material corresponds to the surface covered by nickel and graphite given that the polypropylene is an insulator. Consequently, the fractal dimension value calculated from these data only characterizes the electroactive surface structure covered by both materials. This value is equal to 1.91 and, as a result, the fractional content of nickel plus graphite is around 20% (see Eq. (7)). Thus, and as the fractional content of nickel is around 5%, the fractional content of graphite should be around 15% ($20\% = \text{Ni}\% (5\%) + \text{graphite}\%$).

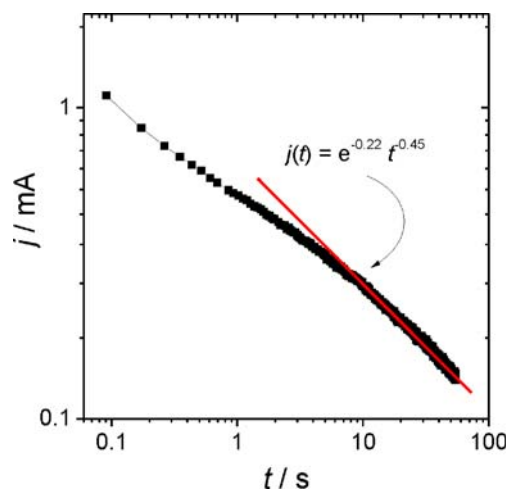


Fig. 4 Chronoamperometry of the anodic electrodisolution of the metallic nickel embedded into the nickel/graphite–polypropylene hybrid composite material. Experimental conditions were 5 mM H_2SO_4 , 0.25 M K_2SO_4 , 5 mM NiSO_4 , and pH 2.0 at -0.78 V. The cell was thermostated at 298 K and bubbled with Ar

From data of environmental scanning electron microscopy, the fractional content of this hybrid composite material is 3% nickel, 13% oxygen, and 84% carbon. At this point, it is important to emphasize that graphite is not a completely inert substance because of the formation of a chemisorbed oxygen layer in the presence of molecular oxygen [24]. This layer should explain the existence of oxygen in the composite material since this is related to the fractional content of graphite. Thus, the experimental fractional content of graphite of this material may be similar to the oxygen content; that is, it may be around 13%. This value confirms the fractional content of graphite estimated electrochemically from Eq. (7) since this is 15%. It is possible to say that Eq. (7) allows to estimate the fractional content of nickel and graphite of the nickel/graphite–polypropylene hybrid composite material.

Conclusion

Electrochemical techniques are here applied to calculate the fractal dimension value of electroactive surface structures of the nickel/graphite–polypropylene hybrid composite material with respect to the experimental conditions. Considering these experimental conditions, the fractal dimension value can be used to estimate the fractional content of nickel and graphite of this composite material by means of the following equation:

$$P(\%) = (4 \cdot 10^{-8})^{-(fd-2)} \quad (8)$$

There is no reason for what this equation may not be applicable for other composite materials. Therefore, and as

the detailed electrochemical procedure is simple, cheap, and quick, it could be introduced as part of the on-line characterization process of composite materials in the composites industry.

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