Original Article

Study of reflection process for nickel coated activated carbon fiber felt applied with electromagnetic interference shielding


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ABSTRACT

Nickel coated activated carbon fiber felt (Ni-ACFF) are known as excellent materials for electrostatic dissipation and electromagnetic interference (EMI) shielding. The deposition of metallic nickel on ACFF was investigated to obtain reproducible and singular materials capable of electromagnetic radiation shielding from 8.2 to 12.4 GHz (X-band). Homogeneous films and fixed quantity of nickel with simple processability were obtained by using the electrodeposition method controlling the experimental parameters, such as, deposition time and current. The relative nickel amount that was controlled from the deposition time and applied current determined the efficiency of reflectivity efficiency with at around 93.7% of the reflected electromagnetic radiation at 8.2 GHz.

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1. Introduction

Over the last decades, materials with EMI properties have aroused a greater interesting from scientific community due to facts related to the growing exigences of governmental control of electromagnetic radiation levels emitted for electronic equipment [1,2]. Industrial standards of electromagnetic compatibility and interference regarding telecom electronic equipment require this demand to enhance their reliability [3]. Besides that, these materials possess a great potential, with attractive applicability on aerospace and aerospace research [4,5] The combination of different materials has been demonstrated to be a new tendency on materials processing, which has permitted an improvement on the performance of electronic devices through the EMI properties1-6.

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Carbon materials, ceramic oxides, conducting polymers and ferromagnetic metals are known to have EMI properties that justify their use as radiation absorber centers. However, the use of these absorbing centers presents as a disadvantage the weight and the volume on the characteristics of the resulting absorber. Materials with EMI based on carbon fibers have been explored to improve such characteristics, since they have a low specific mass that favors its applications in the aerospace industry [6,7].

Carbon materials are known as a good electromagnetic wave reflector [8,9]. The reflection is the main mechanism for EMI, making possible shielding by equipment [5]. However, EMI is not only related to reflection, but also to electromagnetic wave absorption that act as a shield [10]. Yet, there is the mechanism of multiple reflection that happens due to radiation interactions with large surface areas and irregular regions (i.e., porous) [11]. In this sense, EMI refers to the summation of reflection, absorption and multiple reflections contributions related to the existence of free electron charges (electrons or holes) in the material. Thus, the conducting materials tend to have reflection properties. Metallic materials are known by their high electronic conductivity, and among them, nickel (Ni) has aroused great interest due to its low cost and stability [12]. So, these materials can be produced a large induced current under when in action of electromagnetic wave, in conformity with Faraday-Lens’ law this current will be effective in the weakness penetration of the electromagnetic wave, causing a reflection [13-15]

Polyacrylonitrile (PAN) based precursors are fundamental materials to produce high performance carbon fiber felt (CF) for several modern technologies [16]. In particular, the use of the textile PAN precursor as raw material to produce CF presents as advantageous aspects the processing of an inexpensive material, environmental friendly and that structurally permits the conversion into textile form as fabric and non-woven acquiring self-sustainable characteristics [17]. At same time, the substrate graphite structure acquired after the carbonization process and the increase of the porosity resulting of activation process step provide the production of activated carbon fiber felts (ACFF) containing low electric resistivity and high surface area with an uniform micropores distribution, which are fundamental characteristics to be considered for obtaining stable and homogeneous films of metallic Ni [17-20]. These characteristics also have drawn attention of research groups preparing composite materials of EMI applications due to its scientific importance as well for understanding of a new phenomenon attached to them [21,22], as for example, the potential technological application to EMI [23,24]. In this regard, composite materials based on ACFF as matrix for Ni deposition have attracted industrial interest because from it is possible improve the conductivity and also the effect of multiples reflections [15].

Particularly, the choice of the deposition method for producing metallic films on specific substrate is of extreme importance since the quality of the coating depends operational control. Several existing methods are known to deposit metallic films on a substrate that include sputtering, electron-beam evaporation, spraying, hot filament; electroless, chemical methods involving electroless deposition and electrochemical deposition (electrodeposition) [25-27]. Among these, the electrodeposition has their advantageous aspects related to a better control on the thickness, the uniformity and the quantity of the deposited metal, besides of its simplicity and involved low cost.

Based on these considerations, the goal of this work is to obtain high quality nickel on ACFF from electrodeposition method by controlling the current density and the deposition time and to evaluate the EMI on the reflectance an transmittance characteristics for Ni coated ACFF substrates (Ni-ACFF).

2. Experimental

2.1. Nickel-coated Activated Carbon Fiber Felt Production

ACFF samples were produced from Brazilian originated textile PAN and manufactured by following several steps [24]. First, a heavy tow with 5.0 dtex was oxidized in a laboratorial furnace until the fiber came flame resistance. The oxidized tow was cut in 5 cm pieces and converted into felt by standard textile procedure. At the end, the felt (about 100 g m$^{-2}$) was carbonized to 900 °C and activated to 1000 °C in the same furnace by changing the argon gas to carbon dioxide. Micro porosity with specific area of 1300 m$^2$ g$^{-1}$ was verified for produced ACFF (for more details on the ACFF production process [17]).

Prior to electrodeposition of Ni, ACFF were submitted to a cleaning process by acetone immersion and ultrasound sonification for 10 min., followed by a sinking in nitric acid at 40% (v/v) and ultrasound sonification for 15 min. After cleaning, ACFF were exhaustedly washed in deionized water and finally dried at nitrogen atmosphere.

The electrodeposition of Ni on the ACFF substrate was carried out in an aqueous solution containing 0.01 mol L$^{-1}$ NiSO$_4$ 6H$_2$O using a three-electrode electrochemical cell and connected to an AUTOLAB PGSTAT 302 potentiostat/galvanostat. ACFF sample fixed on a Teflon support with exposed geometric area of 8.0 cm$^2$ was used as working electrode. Pt plate was used as auxiliary electrode and Ag/AgCl saturated in 3.0 mol L$^{-1}$ KCl served as reference electrode. The scheme of the electrochemical system used for the electrodeposition of Ni is illustrated in Fig. 1.

The electrodeposition of Ni on the ACFF substrate to produce lightweight materials with EMI properties was conducted by controlling the applied current density and deposition time of Ni. The current densities were defined from the current profile obtained by linear sweep voltammery measurements (not shown) carried out in an aqueous solution containing 0.01 mol L$^{-1}$ NiSO$_4$ 6H$_2$O. The current densities were selected from the current values superior to those involved with the electric layer double formation and established for Ni electrodeposition to occur on the initial stage of the reduction of Ni$^{2+}$ to Ni at different deposition rate. Based on these conditions, the current densities values of -0.1, -0.2 and -0.225 mA cm$^{-2}$ were established to produce Ni with the respective notations Ni-ACFF01, Ni-ACFF02 and Ni-ACFF0225. The deposition time was established to obtain uniform and homogeneous films and controlled content of Ni on the ACFF substrate.

The Ni-ACFF samples were characterized from the morphological analysis using Field Emission Gun - Scanning Electron
Microscopy (FEG-SEM). The FEG-SEM images were acquired on a FEG-SEM FEI Quanta 650 microscopy. The structure characterization was carried out by X-Ray Diffraction (XRD) Spectroscopy for obtaining information about crystalline quality. XRD spectra were recorded in a PANalytical X’PertPRO Diffractometer.

2.2. Measurements of Shielding Effectiveness

The electromagnetic characterization was performed with a X-band rectangular waveguide (Agilent calibration kit WR-90 × 11644A) coupled on a 50 GHz PNA-L vector network analyzer (Keysight N5232A). Electromagnetic properties were measured in the X-band, i.e., from 8.2 to 12.4 GHz. The interaction of the electromagnetic wave on samples was evaluated from the scattering parameters (S-parameters) which give information about the relationship between the reflected and incident power waves at each of the network ports, e.i, $S_{11}$ represents the power reflected from port 1 to port 1 and $S_{21}$ represents the power transferred from port 1 to port 2. Fig. 2 illustrates the scheme of two ports setup used for analyzing the S-parameters and also the representation of these two ports setup in the waveguided form.

The waveguide section was projected with high mechanical precision, in which the electromagnetic wave propagation is launched into a closed system. Basically, the system consists of a waveguide with one terminal the incident electromagnetic wave that can be reflected, transmitted and absorbed. The measured in two ports setup gives information about the energy reflected (R), transmitted (T) and absorbed (A) in the samples [28], as shown in the equation below:

$$1 = R + T + A$$

where R and T are given as $R = |S_{11}|^2$ and $T = |S_{21}|^2$.

It is important mentioning that in this work specifically not was possible calculate the permittivity and permeability of materials through the Nicolson-Ross-Weir (NRW) method, because the $S_{21}$ parameter presented very small values compared with the $S_{11}$.

3. Results and discussion

The quality control of the Ni-ACFF samples was conducted from the morphological analysis that was made by Field Emission Gun - Scanning Electron Microscopy (FEG-SEM) with images acquired on a FEG-SEM FEI Quanta 650 microscopy. Fig. 3 shows the FEG-SEM images for Ni-ACFF produced at different current densities for 4 min. From the FEG-SEM images illustrated in Fig. 2 (b), (c) and (d) is observed that the ACFF was entirely coated by a electrodeposited homogeneous Ni film without, without some surface defect. On the other hand, the FEG-SEM image presented in Fig. 2 (a) can be noticed that no have some present of nickel in ACFF surface though the shine.

Fig. 4 presents FEG-SEM images of a single Ni-ACFF filament in different current densities. Thicker Ni films were electrodeposited on the ACFF as increased the applied current density. The electrodeposited Ni thickness values are presented in Table 1. Despite the increase on the electrodeposited Ni thickness, the shape and the rugosity were unchanged, maintaining the same crystallographic orientation regarding the Ni growth in different applied current densities on ACFF.
Fig. 3 – FEG-SEM images of electrodeposited Ni-ACFF felts in different current densities values (a) ACFF, (b) -0.100 mA cm⁻², (c) -0.200 mA cm⁻² and (d) -0.225 mA cm⁻². Magnification of 1.000x and 30 μm of scale bar.

Fig. 4 – FEG-SEM images of a single Ni-ACFF filament in different current densities values (a) -0.1 mA cm⁻², (b) -0.2 mA cm⁻² and (c) -0.225 mA cm⁻². Magnification of 5.000x and 7 μm of scale bar.

The structural characteristics of the Ni-ACFF samples were analyzed by XRD analysis. Fig. 5 presents the XRD pattern of the electrodeposited Ni on ACFF electrode and five sharp diffraction peaks at 2θ of 44.5°, 51.8° and 76.3° are observed. These peaks correspond to the diffraction from the Ni(111), Ni(002), Ni(220) planes of Ni metal based with the standard crystallographic spectrum of Ni that indicate the metallic form of electrodeposited Ni rather than other Ni species related to oxides or hydroxides, according the JCPDS card number 00-001-1260. It also is possible to observe from the intensity of the diffraction peaks that occurred a decrease on the C(002) peak intensity for the ACFF diffractogram (JCPDS card number 03-065-6212) as increases the thickness of the electrodeposited Ni layer due to increase on the applied current density [29,30]. More information about XRD pattern of the ACFF from the textile PAN precursor are presented in published work by Amaral et al [17].

Fig. 6 represents the reflection and transmission level of the ACFF and Ni-ACFF samples. The graph in the Fig. 6 (a) shows that ACFF sample presents a maximum of 75% for frequencies close to 8 GHz. By increasing the frequency had a decrease on the reflectivity reaching a minimum of 65%. Ni-ACFF 02 sample presented 93.7%, which tends to a constant approximately value for higher frequencies. Ni-ACFF 01 and Ni-ACFF 0225 samples presented initial reflection values around at

<table>
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<th>Table 1 – Thickness values of the Ni film coated on ACFF samples produced at different current densities for 4 min.</th>
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<tr>
<td>Sample</td>
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<tr>
<td>Ni-ACFF 01</td>
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<tr>
<td>Ni-ACFF 02</td>
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<td>Ni-ACFF 0225</td>
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87.0% and 91.6%, respectively, but the reflection level for both samples tends to a constant value of 89% as the frequency increases. An increase on the reflection level as function the increase on the Ni thickness was expected, but, the difficult on the dimensional control of the produced samples to realize the electromagnetic interaction measurements becomes the critical factor that justify the difference in the reflectivity level presented for Ni-ACFF02 sample. Nevertheless, a significative contribution on the reflectivity level compared to ACFF sample is defined by first Ni layer electrodeposited at the initial stages of the process, since the reflectivity level is quasi unchanged as function the increase Ni thickness.

A low transmission level is verified for ACFF as well for Ni-ACFF samples via Fig. 6. This process is explained by bulk characteristic of the ACFF that defines a higher difficult for electromagnetic wave transmission, as can be schematically visualized in in the Fig. 7. This behavior is characterized by multiple reflections process that occurs in the individual filaments that composes the ACFF structure. However, the multiple reflections have a major contribution in the ACFF and provide a greater absorption when compared the Ni-ACFF samples due to the more conducting surface resulting the Ni coating on individual filaments of the ACFF and, therefore, by increasing the reflection level.

Fig. 8 illustrates the absorption level for ACFF and Ni-ACFF samples in a frequency range of 8.2 to 12.4 GHz. The ACFF sample had a absorption level around 22.5% for initial frequencies which increased on high frequencies reaching absorption levels at approximately 35%, whereas the Ni-ACFF samples presented lower absorption levels with values between 5% to 10% of absorption, which demonstrated excellent capability of shielding.

The Ni-ACFF samples had lower absorption values, but higher reflection levels. On the other hand, ACFF sample showed a more significant absorption behavior. Fig. 9 illustrates the possible absorption and reflection mechanism occurring in a single filament into ACFF and Ni-ACFF. As can be
visualized in Fig. 9(a), a possible electromagnetic shielding by reflection process is proposed for Ni-ACFF because the Ni coating difficult the penetration of the electromagnetic radiation inside the single filaments. However, the single filaments in ACFF without the Ni coating permits the incident wave to pass through the filament favoring the electromagnetic shielding by absorption process, as shown in Fig. 9(b).

Some authors have also investigated the influence of metallic films as well in the frequency range of 8-12 GHz [31,32]. Soeth et al. studied the influence of thin titanium films deposited onto a polyethylene terephthalate substrate using sputtering technique to absorb electromagnetic radiation in the rage of 8.2-12.4 GHz. In this work, titanium films with nanometric dimensions in a range of 25 to 400 μm were produced and the electromagnetic wave absorption process was influenced by titanium films with thickness superior to 100 μm which reflected a great part of radiation. This increase of radiation reflection was designated to decrease the electrical resistance. This result agrees with results obtained by us, because by increasing the Ni thickness occurred the decrease on the electrical resistance, allowing more reflection on the electromagnetic radiation. Liu et al. also showed to be possible to improve the shielding properties of a material with the cobalt oxide deposition on carbon fibers by electroless technique. The authors obtained a reflectivity of -40 dB (99.99% shielding) in narrow frequencies. However, these results were calculated for a transmission line model. Previous studies published by Liu et al. [33] evaluated electromagnetic shielding

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**Fig. 8** – Absorbed electromagnetic wave level for ACFF and Ni-ACFF samples. (a) One possible shielding for single filament of Ni-ACFF sample. (b) One possible shielding for single filament of ACFF sample.

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**Fig. 9** – Electromagnetic shielding mechanism for (a) Ni-ACFF and (b) ACFF sample.
using Ni spraying epoxy resin and observed that the material did not have percolation due to the great distance between particulates, making more difficult the energy dissipation. This problem was solved with the addition of Ti$_3$SiC$_2$ particulates improving the conductivity path. The results were satisfying for certain thickness of calculated Ni, shielding up to 99% of radiation in a narrow frequency range. Ni particulates also influenced in a resonance process, allowing an energy dissipation. This behavior was not observed in our results due the fact that nickel was in a film form, and in not particulate form. Besides that, Li et al. [34] studied composites based on Ni/hexagonal ferrite in a polymeric matrix produced with ferrite powder presenting average particle size of about 10–30 μm and Ni powder with dimension around of 2–3 μm for EMI applications. Li et al. also observed that high EMI for samples thickness of 2 mm was predominant by absorption rather than reflection. These results conflict with those obtained by us, where Ni film reflected more electromagnetic radiation than it was absorbed. This conflict occurred because Li et al. used a material formed by pulverized particulates and added ferrite that is known as a good absorber, due to nickel and ferrite in particulate form can cause a loss process by internal multireflection, that is different from the fibers coated by homogeneous nickel layer as in this work. Recently, Yoon-Ji Yim [35] deposited nickel/cooper by electroless on sulfide-polyacrylonitrile (Ni/CuS-PAN) fibers and investigated the EMI properties. The EMI shielding of the Ni/CuS-PAN fibers was significantly improved compared with those as received CuS-PAN fibers. Yim showed that the EMI enhanced as the nickel-plating time increased, with the highest EMI shielding of the 50 min nickel plating at 2.05 GHz with 45 dB (99%) of shielding. According with Yim, nickel layer was a key factor in determining the EMI shielding of the Ni/CuS-PAN fibers due to the electrical conductivity significantly enhanced. Based on these discussions, it is important to observe that the efficiency to shield a material by reflection, by multiple reflection or by absorption, does not depends only of the chemical composition, but also of the used geometry as for example a smooth film, a rough film, a thin film, sprayed and among other possible forms. Furthermore, it is important to mention that the ACFF and Ni-ACFF samples showed good EMI a behavior using the felt form. However, samples with nickel film showed less absorption, due to the metals properties to reflect the radiation in the frequency range of 8-12 GHz, generally associated with their high conductivity. These results would imply that applications would not signal loss, samples with nickel film would be a great option.

4. Conclusions

According the FEG-SEM imagens were observed that ACFFs produced from textile PAN precursor present excellent physic characteristics to be used as composite matrix aiming applications as EMI substrate. Electrodeposition technique was more efficiency for Ni coating on ACFF substrate, whereby homogeneous Ni film was possible to be produced. Besides that, it was observed through electrodeposition technique an increased film thickness nickel as current density enhanced. The Ni thickness contribution on ACFF proved to be significative to reflectivity and the Ni film electrodeposited on the ACFF decreased the absorbed process. The Ni-ACFF 02 sample presented a reflectivity of 93.7% for frequencies close to 8 GHz, and a lower absorption, around of 5%, resulting in good material for EMI. Finally, ACFF in felt form contributed to decrease the signal transmission, since all samples presented a lower transmission, between 1 to 2%, while Ni layer contributed to increase the signal reflection. Thus, important contributions were evidenced from the study of the Ni deposition process on the ACFF, as well as for EMI applications.

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Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES

[34] Li BW, Shen Y, Yue ZX, Nan CW. Applied Physics Letters 2006;89(13):132504.