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Research Progress on Nanostructured Radar Absorbing Materials

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Abstract

Nanostructured radar absorbing materials (RAMs) have received steadily growing interest because of their fascinating properties and various applications compared with the bulk or microsized counterparts. The increased surface area, number of dangling bond atoms and unsaturated co-ordination on surface lead to interface polarization, multiple scatter and absorbing more microwave. In this paper, four types of nanostructured RAMs were concisely introduced as follows: nanocrystal RAMs, core-shell nanocomposite RAMs, nanocomposite of MWCNT and inorganic materials RAMs, nanocomposite of nanostructured carbon and polymer RAMs. Their microwave properties were described in detail by taking various materials as examples.

Keywords: Nanostructured, Radar Absorbing Materials, Nanocrystal, Nanocomposite

1. Introduction

Much attention has been paid to RAMs due to their unique absorbing microwave energy and effectively reducing electromagnetic backscatter so that they are expected to have promising applications in the stealth technology of aircrafts, television image interference of high-rise buildings, and microwave dark-room and protection [1,2]. They are specially designed material to suppress the reflected electromagnetic energy incident on the surface of the absorber by dissipating the magnetic and/or electrical fields of the wave into heat. The excellent RAMs should have certain properties as follows: 1) exhibit strong microwave absorption properties over a wide frequency range; 2) need to be thin and lightweight, especially for aircraft; 3) have simple coating-layer structure and spend less working time during the urgent process. Extensive study has been carried out to develop new microwave absorbing materials with a high magnetic and electric loss [3-5]. Nanostructured RAMs have received steadily growing interest because of their fascinating properties such as absorbing more microwave compared with the bulk or microsized counterparts. Nanostructured RAMs mainly consist of the following four types: nanocrystal RAMs, core-shell nanocomposite RAMs, nanocomposite of MWCNT and inorganic materials RAMs, nanocomposite of nanostructured carbon and polymer RAMs.

2. Nanocrystal RAMs

The surface area, the number of dangling bond atoms and the unsaturated co-ordination on surface are all increased due to the particle sizes of nanocrystals in the range of nanometer. These lead to interface polarization and multiple scatter, which is useful to absorb more microwave. $La_{0.8}Ba_{0.2}MnO_3$ nano-particles (about 80 nm) have microwave absorbing properties both in low and high frequency band in range of 2-18 GHz [6]. The value of microwave absorption in low frequency band is larger than that in high frequency. The microwave absorbing peak is 13 dB at 6.7 GHz and the effective absorbing bandwidth above 10 dB reaches 1.8 GHz for the sample with the thickness of 2.6 mm. The microwave absorption can be attributed to both the dielectric loss and the magnetic loss from the loss tangents of the sample, but the former is greater than the latter. The morphology and size of the nanocrastals play very important roles in the microwave reflection loss (RL) of the nanocrystals. For the nanocrystal $BaFe_{12}O_{19}$ RAMs synthesized under cyclic microwave irradiation [7] from 160 to 760 watts, the degree or extent of the crystallinity of the product increases and the systematic increment in RL appears during irradiation from −4.21 to −14.45 dB and −15.20 to

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−53.69 dB at minimum and maximum frequencies of Ku band respectively. Furthermore, the position of minimum RL peak moves towards higher frequency region and the strongest RL of −53.69 dB takes place at 14.75 GHz for complete grown nano crystals of pyramidal face.

3. Core-Shell Nanocomposite RAMs

To overcome EMI problems, RAMs should have the capability of absorbing unwanted electromagnetic signals so that they should have electric and/or magnetic dipoles which interact with the electromagnetic fields in the radiation. Pure dielectric or magnetic materials are insufficient for absorbing radiation energy. The magnetic–dielectric absorbers of core-shell nanocomposite with suitable dielectric and magnetic properties possess high efficiency because of the complex permittivity and permeability that differ from zero.

The RL of the electroless (Ni-P)/$BaNi_{0.4}Ti_{0.4}Fe_{11.2}O_{19}$ nanocomposite powder [8] in Ku band (12.4 - 18 GHz) is evidently enhanced to −28.70 dB, as compared to the electroless Ni-P nanoglobules (−16.20 dB) and nanocrystalline $BaNi_{0.4}Ti_{0.4}Fe_{11.2}O_{19}$ powder (−24.20 dB). After annealing at 400˚C for 4 h, the RL and bandwidth of electroless (Ni-P)/$BaNi_{0.4}Ti_{0.4}Fe_{11.2}O_{19}$ nanocomposite powder is further improved from −24.20 to −35.90 dB and 1.50 to 4.00 GHz respectively. The RL of the annealed (Ni-P)/$BaNi_{0.4}Ti_{0.4}Fe_{11.2}O_{19}$ nanocomposites powder is improved due to the better match between the dielectric loss and magnetic loss because the combination of amorphous electroless Ni-P and $BaNi_{0.4}Ti_{0.4}Fe_{11.2}O_{19}$ gives the widest bandwidth above −12 dB of 4.00 GHz. The proposed growth mechanism on the bases of characterization results indicates that the deposition onto the nanoparticulate $BaNi_{0.4}Ti_{0.4}Fe_{11.2}O_{19}$ powder of electroless Ni-P layer consists of amorphous electroless Ni matrix, having Ni and Ni_3P nanocrystalline particles to form electroless (Ni-P)/$BaNi_{0.4}Ti_{0.4}Fe_{11.2}O_{19}$ nanocomposite powder.

When the $MnFe_2O_4$ is coated with the TiO_2 completely, the composites have good compatible dielectric and magnetic properties and hence the microwave absorbing properties show the maximum value. The representative $MnFe_2O_4$–TiO_2 nano-composites [9] exhibit super-para magnetic behavior resulting from $MnFe_2O_4$ nanoparticles and the enhanced imaginary parts of permeability due to the eddy loss of semiconductor TiO_2 nanoparticles. The complex permittivity and permeability of $MnFe_2O_4$ and $MnFe_2O_4$–TiO_2 composites measured in the microwave frequency range of 2 - 10 GHz show that the microwave absorption properties of the $MnFe_2O_4$–TiO_2 composites are higher than that of $MnFe_2O_4$.

Additionally, the tanδ of the cupric oxide-nanowire-covered carbon fibers (CNWCFs) shows two peaks when the frequency ranges are 4 - 13 and 14 - 18 GHz, respectively, which indicates wide range microwave absorption in both frequency ranges according to the microwave absorption theory. The absorption frequency and bandwidth of CNWCFs decrease with the thickness increaseing and the optimum thickness of CNWCFs is 1 - 1.3 mm [10]. The reflectivity of CNWCFs (1mmin thickness) is less than −4 dB over the range of 11.8 - 18 GHz and −10 dB over the range of 13.5 - 16 GHz, while the reflectivity of CNWCFs (1.3mm in thickness) is less than −4 dB over the range of 8.6 - 15 GHz and −10 dB over the range of 9.8 - 13 GHz.

4. Nanocomposite of MWCNT and Inorganic Materials RAMs

Although ε_r'' of the purified MWCNTs is larger than 40 between 2 and 18 GHz and even exceeds 100 at lower frequencies, the RL still remains rather small, because another important parameter relating to RL is the concept of matched characteristic impedance, where the characteristic impedance of the absorbing material should be made nearly equal to that of the free space (377 $\Omega \cdot sq^{-1}$) to achieve zero-reflection at the front surface of the material [11]. Nanocomposite of MWCNT and inorganic materials could be good candidate because the combination of both materials brings about better matched characteristic impedance and improved RL.

Although the RL of purified MWCNTs keeps constantly at 1 dB except for a small peak of 1.23 dB at 2.8 GHz, the RL of MWCNT filled and surface decorated with γ-Fe_2O_3 is larger than 3 dB between 5 and 18 GHz with a maximum of 5.32 dB at 7.0 GHz. When γ-Fe_2O_3 is transformed to Fe/Fe_3C by heat-treatment in H_2 atmosphere at 950˚C [12], the microwave absorption of the Fe/Fe_3C–MWCNT composite is enhanced greatly at all frequencies between 2 and 18 GHz so that the RL is larger than 3 dB between 4.6 and 18 GHz with a maximum of 12.57 dB locating at 9.2 GHz. This result from enhanced magnetic loss and better matched characteristic impedance, rather than electric loss, as shown by the complex relative permeability and permittivity. The frequency corresponding to the maximum RL of Fe/Fe_3C–MWCNT composite shows an inverse relationship with the increase in its thickness and the maximum attenuation of the incident wave is increased from 11.00 (12.40 GHz) to 13.88 (4.60 GHz) when the thickness is increased from 1.5 to 3.5mm. The microwave absorbing properties can be modulated simply by manipulating the thickness of the prepared Fe/Fe_3C–MWCNT composite for application in different frequency bands.

The Er_2O_3 nanoparticles encapsulated in the cavities of

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MWCNTs could also modulate the electromagnetic parameters of MWCNTs, and thus affect the microwave absorbing properties. The Er_2O_3-filled MWCNTs possess much broader absorbing bandwidth and larger reflectiveity, complex permeability and magnetic loss tangent than unfilled MWCNTs [13]. The maximum absorbing peak of raw MWCNTs is about −21.58 dB at 9.4 GHz in the range of X wave band with the thickness (dm) of 2.0 mm, the bandwidth of the reflectivity below −5 dB is 3.50 GHz and the bandwidth of the reflectivity below −10 dB is 1.58 GHz. In contrast, under the same matching thickness (dm = 2.0 mm), the maximum absorbing peak of the Er_2O_3-filled MWCNTs increases to −27.96 dB and shifts to 10.0 GHz, the bandwidth of the reflectivity below −5 dB is 4.65 GHz and the bandwidth of the reflectivity below −10 dB is 2.30 GHz. With the increase of thickness, the peak value of reflectivity shifts to lower frequencies and multiple absorbing peaks appear.

There are three reasons for the improved absorbing performance of Er_2O_3 modified MWCNTs as follows: firstly, the specific location of the Er ion in MWCNTs could generate a charge effect [14] and RE oxide located in MWCNTs cavities could change the microenvironment of the resonators MWCNTs; secondly, the energy levels of the nanosized Er_2O_3 crystals encapsulated in one-dimensional MWCNTs are not continuous but discrete because of quantum confinement effect according to Kubo theory; finally, the Er^{3+} ion has the [Xe] 4f configuration, the 5d shell is empty and there are three unpaired 4f electrons interacting with the crystalline environment. The electron magnetic moment may cause a large magnetic loss in the composite.

5. Nanocomposite of Nanostructured Carbon and Polymer RAMs

Carbon nanotubes (CNTs) as conductive filler have been widely studied in RAMs due to their physical and chemical properties such as light weight and strong microwave absorption properties in the GHz frequency range [15]. For CNTs/polymer (PET, PP, PE and varnish) nanocomposites [16], the position of reflectivity peak moves to a lower frequency and the loss factors of composites increase with increasing CNTs concentrations. At the CNTs concentration of above 4 wt%, loss tangent of the composites sharply increases because this behavior corresponds to a phase transition from an insulator to a conducting composite at this concentration and a drastic change in the electrical resistivity with a corresponding change in the behavior of its electromagnetic characteristics. Polymer matrix has an obvious effect on microwave absorbing properties. CNTs/PET composite achieves a maximum absorbing value of 17.61 dB and RL of over 5 dB between 5 GHz and 18 GHz, while the maximum absorbing value of CNTs/varnish composite is 24.27 dB. However, CNTs/PE composite has a maximum absorbing value of 8.01 dB when CNTs concentration is up to 8 wt%. In addition, the frequencies range for absorbing values exceeding 5 dB of CNTs/(PET, PP, varnish) composites are 13 GHz, 10 GHz and 6 GHz, respectively. The microwave absorption of CNTs composites can be mainly attributed to the dielectric loss rather than magnetic loss because the value of dielectric loss is much higher than that of magnetic loss especially in frequentcies ranging from 6 GHz to 18 GHz.

Compared to the raw GFR (Glass Fiber–Reinforced) composites (G8, G16) with low absorbing efficiency, the GFR nanocomposites consisting of glass fiber, epoxy and nanosized carbon materials such as CB (carbon black) 16, MWCNT8 and MWCNT16 show outstanding absorbing efficiency over 10 dB between 8 and 12 GHz frequency range (as shown in **Figure 1**). Especially, the GFR–MWCNT composite with 16 plies (MWCNT16) provides three times higher efficiency than those of CB composites (CB16) [17].

When the onion-like carbon (OLC) is dispersed in different polymer matrix such as PMMA and epoxy [18], the EM reflection provided by OLC is higher when embedded into PMMA host matrix because the higher adhesion of PMMA and OLC agglomerates provide formation of more homogeneous distribution of OLC within polymer matrix. OLC content essentially influences the EM absorption for OLC/PMMA films: the EM attenuation increases as much as 2.5 times with the increasing of OLC concentration from 2 to 20 wt% for whole frequency range. More efficient shielding properties have been observed for OLC aggregates of the smallest sizes as compared to larger-sized aggregates at the same OLC loading, as is attributed to the better dispersion and formation of a continuous conductive network by smaller aggregates (reaching the significantly lower percolation threshold) [19].

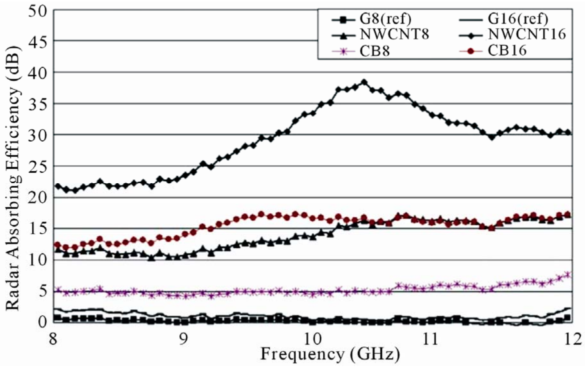

Figure 1. Comparison of radar absorbing efficiency for raw GFR and GFR nanocomposite.

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For E-glass/epoxy composite laminates containing three different types of carbon nano materials such as carbon black (CB), carbon nanofiber (CNF) and multiwall carbon nanotube (MWNT) [20], the real and imaginary parts of the complex permittivities of the composites are proportional to the filler concentrations. Depending on the types of fillers and frequency band, the increasing rates of the real and imaginary parts with respect to the filler concentrations are all different with the order of CNF > MWNT » CB. These different rates can have great effect on the thickness in designing the single-layer microwave absorbers and the order of thickness of composite materials at their optimums is CNF < MWNT « CB. The excellence of CNF originates from its high conductivity and straightness offering the possibility of big electric dipoles and inducing higher dielectric constant of composites.

The mixed type absorbers employing two fillers for both dielectric and magnetic characteristics are possible candidate materials for overcoming the narrow absorption of dielectric RAMs and heavy weight of magnetic RAMs. The mixed RAMs containing carbon nanofibers (CNFs) as dielectric lossy materials to increase permittivity and NiFe particles as magnetic lossy materials [21] show improved absorbing characteristics with thinner matching thicknesses. The present mixed RAMs show the 10 dB absorbing bandwidth of 4.0 GHz in the X-band (2.00 mm thickness) and 6.0 GHz in the Ku-band (1.49 mm thickness).

6. Conclusions

Nanostructured RAMs possess enhanced absorbing property due to the nanometer size. The morphology and size of the nanocrastal RAMs play very important roles in the microwave RL of the nanocrystals and, as the degree or extent of the crystallinity increases, the systematic increment in RL appears. The magnetic-dielectric absorbers of core-shell nanocomposite RAMs with suitable dielectric and magnetic properties possess high efficiency because of the complex permittivity and permeability that differ from zero. Nanocomposite of MWCNT and inorganic materials RAMs combines better matched characteristic impedance and improved reflection loss of both materials. For nanocomposite of CNTs and polymer RAMs, the position of reflectivity peak moves to a lower frequency and the loss factors of composites increase with increasing CNTs concentrations. More efficient shielding properties had been observed for OLC aggregates of the smallest sizes as compared to larger-sized aggregates at the same OLC loading. The increasing rates of the real and imaginary parts for nanocomposite of nanostuctured carbon and polymer RAMs with respect to the filler concentrations depend on the types of fillers and frequency band.

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