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Electromagnetic interference shielding effectiveness of high entropy AlCoCrFeNi alloy powder laden composites

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The electromagnetic interference (EMI) shielding effectiveness of epoxy based composite samples, containing two different sizes of high entropy AlCoCrFeNi alloy powders, was examined under Kα band [26–40 GHz] in this paper. High-energy ball milling processes were used to fabricate AlCoCrFeNi alloy powders of two different sizes, HEA_L for larger sizes and HEA_S for finer powders, respectively. Comparing with the 8.44 dB value of the HEA_L containing sample, the HEA_S sample has a maximum total shielding effectiveness (SE_T) of 20 dB due to the smaller powder sizes and flake-like morphology. Shielding mechanism was studied by resolving the total EMI SE_T into absorption and reflection portions. Absorption was found to be the major shielding mechanism and reflection had a secondary shielding effect for both HEA_L and HEA_S cases.

1. Introduction

Electromagnetic interference (EMI) is a concern for both the reliable operation of systems/devices, such as satellites, autonomous vehicles, wireless data transfer devices, radars, etc. and the safety of the human living space [1], as EMI may interrupt the desired functionality of electric appliances and pose a health issue to general public. To mitigate the EMI problem, a common approach is to isolate the systems using a lightweight wide frequency band shielding material. The frequency range in Kα band [26–40 GHz] is important for many applications, e.g. radar and satellites operating in this frequency range [2]. EMI shielding effect is caused by two main mechanisms: reflection and absorption. For good reflection, the shielding materials must have mobile charge carriers (electrons or holes) for an effective interaction with the incoming electromagnetic fields. Consequently, metals and alloys are widely applied for shielding of electromagnetic radiations due to a high value of electrical conductivity [3,4]. Absorption is another EMI shielding mechanism, where electric and/or magnetic dipoles interact with the electric and magnetic vectors of the incident EM radiation. Electric and magnetic dipoles are commonly found in materials with high values of dielectric constant and magnetic constant. In this regard, magnetic metals (Fe, Co, Ni and ferrite etc.) are attractive candidates. Compared with pure metals, the GHz permeability of ferromagnetic alloys with high saturation magnetization is superior due to their higher Snoek's limitation frequency [5]. Therefore, ferromagnetic alloys, especially the ferromagnetic alloy nano powders containing Fe, Co, and Ni are promising candidates for the EMI applications.

To obtain a good EMI shielding effectiveness, metals are usually applied onto a substrate using a variety of processing methods. Gargama et al. [6] made polyvinylidene fluoride/nanocrystalline iron composites with mechanical blending and hot-molding method; Ziaja et al. [7] prepared Ti and brass alloy coatings onto a nonwoven polypropylene substrate using DC sputtering; Combining both magnetron sputtering and vacuum-assisted resin transfer molding methods, Xia et al. [8] coated copper films onto kenaf fiber reinforced composites; Kim et al. [9] applied an electroplating method to obtain Ni-Co/carbon fibers-reinforced composites. Bi et al. [10] applied electroless plating and an alkoxy silane self-assembly method to make conductive fabrics with desired EMI shielding effectiveness; Electroless deposition method was also used by Shi et al. [11] to coat Ni–Mo–P ternary alloy onto birch veneers to make EMI shielding and corrosion-resistant wood composites; Solution blending method was used by Ren et al. [12] to prepare EMI shielding composites with a combination of graphene nanosheets and nickel ferrite ($NiFe_2O_4$); Hot pressing

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coupled with diffusion treatment was used by Ma et al. [13] to make ferro-aluminum based sandwich composites for EMI shielding applications. For high temperature applications, chemical vapor infiltration was used by Mu et al. [14] to fabricate SiC_f/SiC composites with BN interphase for EMI shielding applications at a temperature up to 700 °C; Wen et al. [15] applied plasma spraying method to make $MoSi_2$/glass composite coatings with different $MoSi_2$ content; Al–Si alloy infiltration based densification process was developed by Fan et al. [16] to fabricate C/SiC–$Ti_3Si(Al)C_2$ EMI shielding materials; Li et al. [17] used divinyl benzene to modify a polycarbosilane precursor for making graphene-like carbon-silicon carbide nanocomposites, which were examined for EMI shielding effectiveness up to 600 C in air.

New alloy fillers were also examined for EMI shielding applications. For example, Liu et al. [18] examined Mg–Zn–Zr–Ce alloys. EMI shielding effectiveness was found to be improved initially with the addition of Ce, and then decreased. Chen et al. [19] reported that with Nd element addition, both mechanical properties and EMI shielding capacity were enhanced significantly for Mg-Y-Zr-xNd alloys. Yang et al. [20] examined the effects of Sm addition on EMI property of Mg–Zn–Zr alloys. The precipitation of Sm-containing rare earth phases is believed to be the reason for EMI shielding improvement.

In this paper, multi-principle alloys or high entropy alloys (HEA) were examined for EMI filler application. The high entropy alloy (HEA) concept was first proposed by Yeh et al. [21] and developed in recent years by many researchers. The HEA approach employs five or more principal elements in near equimolar ratios in a solid solution, with atomic percentage of each element varying between 5% and 35%. With multiple principal elements, HEAs usually have extraordinary phase stability due to the increased configurational entropy, inciting a fascinating new area in metallurgy. Unlike the traditional alloys, which have a single principle element in conjunction with a few alloying elements, HEAs have the potential to combine the desirable properties of several different base elements according to the “cocktail effect” [22]. HEAs has exhibited high strength [23–25], outstanding wear resistance [26,27], good thermal stability [26,28] and corrosion resistance [29,30] in previous studies. However, the studies of HEAs are, so far, mostly limited within mechanical properties. Up to now, very limited investigations on EMI shielding effectiveness of high entropy alloys do show a good potential for using HEAs as EMI shielding materials. Yang et al. [31] demonstrated the fabrication of flaky shaped FeCoNiCrAl HEA powders through mechanical alloying and studied the EMI performance over the range of 2–18 GHz for a high powder content (70 wt% powders) mixture with paraffin matrix. Same group also examined the effect of phase structures of FeCoNiCrAl0.8 HEA powders to electromagnetic wave absorption properties [32].

In this study, the EMI shielding effectiveness of HEA powders of different sizes and morphologies is examined. The equimolar AlCoCrFeNi alloy was chosen as a starting point to investigate the EMI shielding effective. Since many AlCoCrFeNi HEA systems with non-equimolar compositions have been reported to have excellent structural properties [33,34], the EMI performance for non-equimolar composition AlCoCrFeNi alloys, such as by altering the Al or Ni elemental contents, will be examined in future studies.

2. Experimental

Being a typical technique for the preparation of alloy powders, high energy ball milling was adopted in this study to synthesis the solid solution HEA powders. Using dry milling, usually only large sized powders can be obtained even after an extended milling time because the crushed powders have the tendency of being cold welded again during the process [35]. The intrinsic microwave properties of alloy powder laden composites are believed to depend on the powder sizes, crystal structures, grains and the boundary conditions [36,37]. Therefore, after the large sized AlCoCrFeNi powders (HEA_L) were obtained, wet ball milling was further employed to reduce the powder size. In this paper, epoxy based composites, containing either large AlCoCrFeNi powders (HEA_L) or small AlCoCrFeNi powders (HEA_S), were evaluated for EMI shielding performance. The microstructure and chemical compositions of HEA_L and HEA_S were firstly characterized by the XRD, SEM, EDS, and HRTEM. The electromagnetic shielding effectiveness and absorption performance of HEA_L and HEA_S filled epoxy composites were investigated in the Ka-band, to examine the impact of particle sizes to the EMI shielding effectiveness.

2.1. Material

The following elemental powders were used to form HEA powders: Aluminum (Al< 40 μm, Sigma-Aldrich, 99.5%), Chromium (Cr < 40 μm, Sigma-Aldrich, 99.5%), Iron (Fe < 40 μm, Alfa Aesar, 99.5%), Cobalt (Co < 40 μm, Sigma-Aldrich 99.5) and Nickle (Ni < 10 μm, Sigma-Aldrich, 99.9%). The epoxy resin was purchased from a commercial source (AeroMarine, USA) along with the curing agent #21.

2.2. High entropy alloy powder preparation

The high-energy ball milling (HEM) technique is a common process to produce micro, and nano-sized powders or flakes. The base of HEM synthesis is the strong mechanical energy transfer created by colliding hard phase materials, such as ceramic or hard alloy balls, with reactants such as metals, alloys, and composites. During the HEM process of high entropy alloy powders, multiple fracturing and welding ensure that the milling operations will lead to the solid-state reaction of the elemental powders, resulting in the formation of the final high entropy alloy [38]. Fig. 1 illustrates the formation mechanism of HEA powders using HEM synthesis. High purity elemental powders of Al, Cr, Fe, Co and Ni with the same atomic percentage were homogeneously mixed, and then put into a stainless steel mill vial together with stainless steel balls (8 mm and 12 mm in diameter and 1:4 in weight ratio). The weight ratio of the powders to the grinding ball was 1:5, and the large HEA powders (HEA_L) were obtained after ball milling for 10 h. Subsequently, 5 h of wet ball milling was applied to reduce the sizes of the large HEA powders. The milling process, and the handling of both the raw materials and the milled products, were carried out in an argon gas environment inside a glove box to protect the powders from oxidation.

2.3. Preparation of HEA/epoxy composites

The purpose of this step was to generate HEA_L (20 vol %) and HEA_S (20 vol %) filled epoxy samples, to be used for EMI shielding evaluations. The desirable amount of HEA_L powders or HEA_S powders was firstly dispersed into the epoxy resin monomers, which were allowed to completely wet the powders overnight without any disturbance [39]. Then the suspension was mechanically stirred for 1 h at 600 rpm for uniform dispersion and was followed by one additional hour of sonication, which was essential to remove the bubbles trapped in the early processes from the suspension. The curing agent was then added to the powders-epoxy mixture with a monomer/curing agent volume ratio of 1/1, as recommended by the AeroMarine Product Company. Low-speed (300 rpm) mechanical stirring was conducted on the curing mixtures for 20 min at room temperature to further disperse the powders and mix the epoxy and curing agent well. Then sonication