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Magnetoelastic properties of epoxy resin based $Tb_xHo_{0.9-x}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ particulate composites

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$Tb_xHo_{0.9-x}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ ($0 \leqslant x \leqslant 0.40$) particulate composites were prepared by embedding and aligning alloy particles in an epoxy matrix with and without a magnetic curing field. The magnetoelastic properties were investigated as functions of composition, particle volume fraction and macroscopic structure of the composite. The magnetic anisotropy compensation point was found to be around x = 0.25, where the easy magnetization direction (EMD) at room temperature was detected lying along ⟨1 1 1⟩ axis. The composite with ⟨1 1 1⟩ preferred orientation and pseudo-1-3 type structure was prepared under an applied magnetic field of 12 kOe. An enhanced magnetoelastic effect and large low-field magnetostriction λ_a, as high as 430 ppm at 3 kOe, were obtained for $Tb_{0.25}Ho_{0.65}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ composite rod. The value of λ_a was of 72 % of its polycrystalline alloy (~595 ppm/3 kOe) although it only contained 30 vol.% of the alloy particles. This enhanced effect can be attributed to the larger λ_{111} (as compared to λ_{100}), low magnetic anisotropy, easy magnetization direction (EMD) along the ⟨1 1 1⟩ axis and ⟨1 1 1⟩-textured orientation of the alloy particles as well as the chain-like structure of the composite. The good magnetoelastic properties of the composite, in spite of the fact that it contained only 30 vol.% of the alloy particles with light rare-earth Nd element in the insulating epoxy, would make it a potential material for magnetostriction application.

Keywords: *magnetostriction; magnetostrictive composite material; X-ray diffraction; magnetic properties*

1. Introduction

Pseudobinary Laves phase $R'RFe_2$ (R, R' = rare earth) compounds, e.g., $Tb_{0.27}Dy_{0.73}Fe_2$ (Terfenol-D) and $Tb_{0.15}Ho_{0.85}Fe_2$, have been recognized as important magnetoelastic materials for application in ultrasonic generators, stress sensors and actuators [1, 2]. However, the eddy current loss is a crucial problem in monolithic alloy materials, which limits their applications around a few kHz. Another problem is intrinsic mechanical brittleness and formability, causing difficulties in device fabrication. In response to these shortcomings, some significant efforts in the past decade have been devoted to the study of polymer composite system [3–7]. It was reported that the epoxy-bonded particulate composite, by combining alloy particles with a passive epoxy matrix, has demonstrated additional benefits, e.g. reduced eddy-current loss and robust mechanical properties, which broadened its application at a high frequency range up to ultrasonic regime and made it a useful durable material accommodating tensile and stress loading states.

Although the monolithic alloy and composite of Terfenol-D are practical materials due to high magnetostriction and low magnetic anisotropy, they are not cost-effective enough for commercial applications because Terfenol-D consists mostly of heavy rare earths, Tb and Dy, which are both expensive and scarce in the earth crust. Therefore, a novel magnetostrictive compound based on the lower-cost light rare earth is highly desired. Recently, the development of Laves alloys containing Nd element has been a hot research topic, owing to $NdFe_2$ possessing a large theoretical magnetostriction ($\lambda_{111} \sim$ 2000 ppm at 0 K) and a low magnetic anisotropy [1, 8, 9]. In our previous experimental study, we have succeeded in synthesizing the single-phase $Tb_xHo_{0.9-x}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$

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alloys, which had good magnetoelastic properties [10]. The aim of the present work, is to extend our previous work on these compounds to fabricate epoxy resin based 0-3 and 1-3 type particulate composites for the realization of their macroscopic magnetic and magnetoelastic properties, and correlate them with the macroscopic structure of the composites. In addition, the effect of composition, easy magnetization direction (EMD) and particle volume fraction (V_f) on magnetostriction and textured orientation structure is presented in order to understand the magnetoelastic properties of the composite.

2. Experimental

All polycrystalline alloys with the nominal compositions $Tb_xHo_{0.9-x}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ of $0 \leqslant x \leqslant 0.40$ were prepared by arc melting of appropriate constituent metals with a purity of 99.9 wt.% in a high-purity argon atmosphere [10]. Subsequently, the ingots were sealed in an evacuated quartz tube filled with high-purity argon and treated at 650 °C for 9 days for homogenization, and then the furnace was cooled to room temperature (RT). The homogenized ingots were ground into particles with randomly distributed sizes. Particle segregation was achieved using sieves with a size distribution range of 60 μm to 150 μm. X-ray diffraction (XRD) data was recorded at RT with CuKα radiation in a D/max-γA diffractometer equipped with a graphite crystal monochromator.

As for the particulate composites, an epoxy-resin bonding route has been used to produce rod samples [11]. Predetermined quantities of alloy particles and epoxy resin (Araldite LY1564/ Aradur 3487, tensile modulus of 3200 MPa to 3350 MPa) were homogeneously mixed in a plastic mold. Subsequently, the resulting mixture was degassed under a vacuum for 30 min to eliminate the trapped air bubbles. The moulds were then sealed to prevent particles from migrating out and placed in air for solidification without stress. This composite was classified as the 0-3 type one, in which the embedded alloy particle phase was isolated and the epoxy matrix phase was connected in all three directions. For comparison, the moulds were placed in an electromagnet for 8 hours for solidification. A uniform DC magnetic field of 12 kOe was provided along the longitudinal direction of the moulds, causing the particles to align with the direction of magnetic field and producing particulate chains similar to pseudo-fiber composites (classified as pseudo-1-3 type composites), in which the embedded alloy particle phase was connected in one direction and the second phase of epoxy matrix was connected in all three directions [7, 11]. The particle volume fraction of the composite was determined based on Archimedes principle and the rule-of-mixture formulation for density as:

$$\rho_c = V_f \rho_a + (1 - V_f)\rho_e \tag{1}$$

where ρ_c, ρ_a and ρ_e are the densities of composite, alloy and epoxy resin, respectively, and V_f is the particulate volume fraction of the composite. The macroscopic observations of textured orientation structure of the composites were also performed by using XRD. The magnetostrictions ($\lambda_{\parallel}$ and $\lambda_{\perp}$) parallel and perpendicular to the applied field were measured without pre-stress at RT by using a static resistance strain gauge. The magnetization measurements were carried out at RT by using a vibrating sample magnetometer (VSM) up to an applied magnetic field of 20 kOe.

3. Results and discussion

XRD analysis confirms that the homogenized $Tb_xHo_{0.9-x}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ ($0 \leqslant x \leqslant 0.40$) alloys are composed essentially of C15 single-Laves phase in the whole investigated concentration range. As an example, the XRD pattern of random powders of $x = 0.25$, is shown at the bottom panel of Fig. 1. All reflections are in accordance with the characteristics of C15 structure, and the indices (h k l) of the pseudo-cubic Laves phase are indexed. As for the 0-3 type composite with 30 vol.% alloy particles, the phase structure did not change except for the diffraction intensity which decreased slightly since the alloy particles were randomly dispersed in the epoxy matrix. For the pseudo-1-3 type composite, XRD was carried out

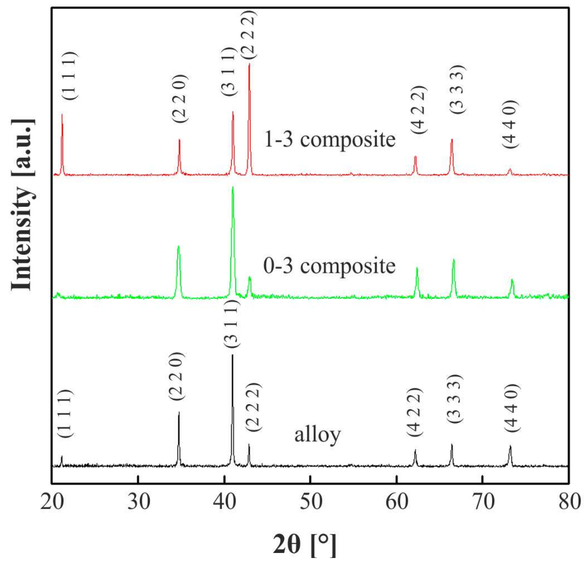

Fig. 1. XRD patterns of the $Tb_{0.25}Ho_{0.65}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ alloy and the composites.

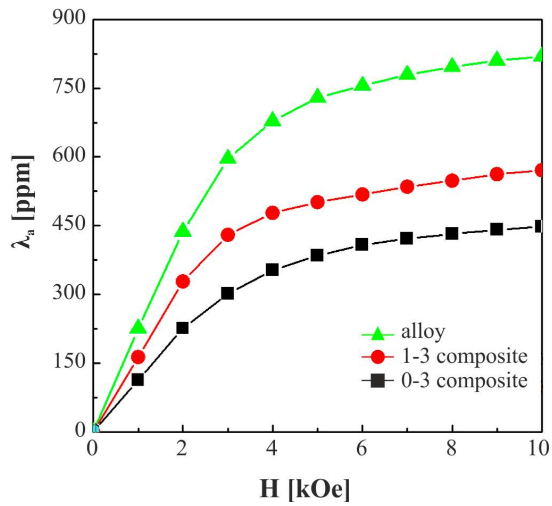

Fig. 2. Magnetic field dependence of linear anisotropic magnetostriction λ_a $(= \lambda_{\parallel} - \lambda_{\perp})$ for the $Tb_{0.25}Ho_{0.65}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ alloy and composites.

on the surface (perpendicular to the direction of the curing magnetic field) of the samples. It is seen that the intensity of the (2 2 2) peak is the strongest, additionally accompanied by the strengthened (1 1 1) and (3 3 3) peaks. Thus, the ⟨1 1 1⟩ direction may be its easy magnetization direction (EMD), which is consistent with the analysis of crystal structure distortion. It seems that the rhombohedral distortion is related to a large spontaneous magnetostriction coefficient λ_{111} [1, 10]. The magnetic field dependence of linear anisotropic magnetostriction $(\lambda_a = \lambda_{\parallel} - \lambda_{\perp})$ is presented in Fig. 2. We can see that while the pseudo-1-3 type composite contains only 30 vol.% alloy particles, λ_a approaches 72 % of the corresponding alloy value at the same field level. As an example, at $H = 3$ kOe, λ_a of 430 ppm is achieved compared with the value of 595 ppm for the alloy. In addition, the 1-3 type composite has a larger magnetostriction as compared to 0-3 composite. This λ_a enhancement effect can be ascribed to the magnetization nature (Fig. 7) of the embedded anisotropic alloy particles, the textured orientation structure (Fig. 6) as well as the grain-aligned chain structure (i.e. 1-3 type configuration) of the composite wherein magnetostriction could be transferred through the interaction of the neighboring alloy particles [4].

To understand the dependence of the optimal magnetostrictive properties on the alloy composition x, the magnetostriction λ_a for the 1-3 type $Tb_xHo_{0.9-x}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ composites with 30 vol.% alloy particles was measured in a stationary state at an applied magnetic field up to 10 kOe, as shown in Fig. 3. It is seen that the saturation has not been achieved for all the samples, however, the approached saturation appears more pronounced for $x = 0.25$ than for the other compositions, indicating its lower magnetic anisotropy. This behavior is similar to that of its mother alloy, in consistence with the minimum magnetic anisotropy of the alloy system with $x = 0.25$ [10]. For clarity, the curve $\lambda_a = f(x)$ at various magnetic fields is plotted in Fig. 4. It is obvious that λ_a at different magnetic fields exhibits a peak near $x = 0.25$, implying the minimum magnetic anisotropy. The trend in the behavior of all the alloys with different x, suggests their low magnetic anisotropy caused by the anisotropy compensation between Tb^{3+} and Ho^{3+} ions [10].

To further study the effect of particle volume fraction V_f on magnetostriction, the 1-3 type $Tb_{0.25}Ho_{0.65}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ composites with different V_f ranging from 10 to 48 vol.% were

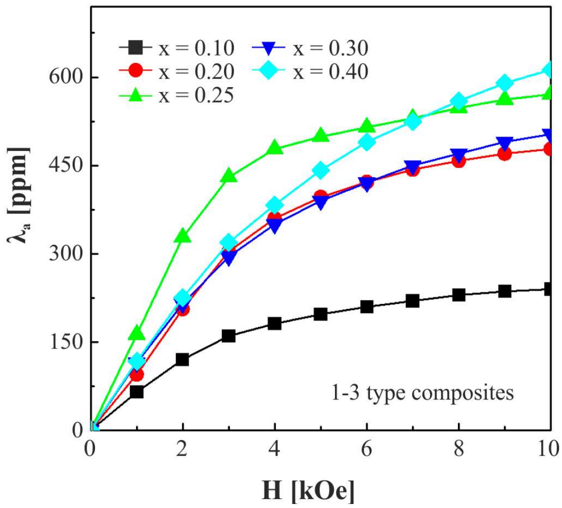

Fig. 3. Magnetic field dependence of linear anisotropic magnetostriction λ_a $(=\lambda_{\|}-\lambda_{\perp})$ for the 1-3 type $Tb_xHo_{0.9-x}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ composites with 30 vol.% alloy particles.

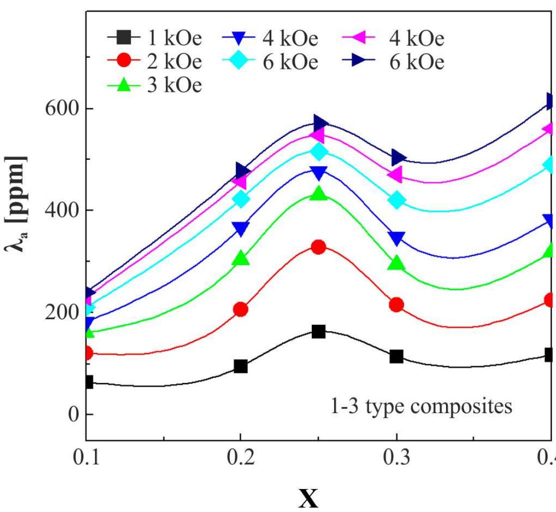

Fig. 4. Compositional dependence of linear anisotropic magnetostriction λ_a $(=\lambda_{\|}-\lambda_{\perp})$ for the 1-3 type $Tb_xHo_{0.9-x}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ composites with 30 vol.% alloy particles.

fabricated. The linear anisotropic magnetostriction $\lambda_a(=\lambda_{\|}-\lambda_{\perp})$ versus magnetic field strength is presented in Fig. 5a. λ_a at the same measured field increases with increasing V_f up to 30 vol.%, and then it drops, presenting the largest value for 30 vol.%. Compared with the sample of 30 vol.%, the lower λ_a for the lower V_f (10 vol.% or 20 vol.%) may be due to the dilution effect of the nonmagnetic epoxy matrix. However, λ_a decreases with further increasing V_f when it is larger than 30 vol.%. The similar tendency has been found for epoxy-bonded Terfenol-D composites, which has been ascribed to the poor contact between particles due to their close packing in a certain space [4]. In addition, the higher volume fraction leads to the lowering of the degree of textured orientation structure compared to the sample of $V_f \sim 30$ vol.% and lower V_f ($\sim$10 vol.% or 20 vol.%). In other words, the higher V_f inhibits the irregular particles rotation along the curing field during forming the textured orientation structure in the composite, which is consistent with the XRD patterns presented in Fig. 6. The saturation linear anisotropic magnetostriction λ_{0S} was estimated by the law of approach to saturation as [11]:

$$\lambda_a(H) = \lambda_{0S}\left(1-\frac{a_0}{H}\right) \qquad (2)$$

where a_0 is a constant. The relation between the alloy particle content and λ_{0S} is shown in Fig. 5b. As can be seen, λ_{0S} increases with increasing the volume fraction up to 30 vol.%, reaching the maximum value of 570 ppm, and then it drops.

To understand the impact of textured orientation structure on magnetostrictive properties of the composites, XRD study was performed on the surface (perpendicular to the direction of the curing magnetic field) of the 1-3 composite, as shown in Fig. 6, where the $Tb_{0.25}Ho_{0.65}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ composites with different volume fractions are presented. It can be observed that the $\langle 1\ 1\ 1\rangle$-type peaks, such as (2 2 2) or (3 3 3), are much higher compared with similar peaks in the randomly distributed powders, in which the intensity of (3 1 1) peak appears the strongest (Fig. 1). This shows that the $\langle 1\ 1\ 1\rangle$ easy magnetic axis of each grain is aligned along the direction of the orientation field, namely, the curing field causes the grains to rotate in order to align their EMD $\langle 1\ 1\ 1\rangle$ axes along this field. Furthermore, the intensity ratio $I_{(222)}/I_{(311)}$, an indicator of the magnetocrystalline alignment, is different for various V_f, indicating the difference in the degree of $\langle 1\ 1\ 1\rangle$ alignment. The value of $I_{(222)}/I_{(311)}$ decreases with increasing

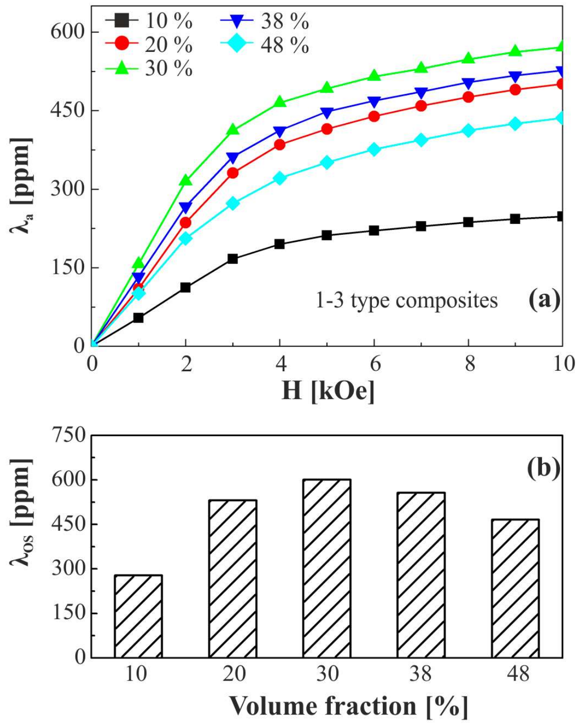

Fig. 5. (a) Magnetic field dependence of linear anisotropic magnetostriction λ_a $(= \lambda_{\parallel} - \lambda_{\perp})$ for the 1-3 type $Tb_{0.25}Ho_{0.65}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ composites with various particle volume fraction; (b) particle content dependence of the saturation magnetostriction λ_{0S}.

V_f, corresponding to the decrease in alignment degree along ⟨1 1 1⟩ direction. In other words, more alloy particles embedded in the matrix may inhibit their rotation. The dependence of λ_a on V_f, as well as the λ_a enhancement effect (Fig. 2), can be explained by the equation for the magnetostriction of a polycrystalline alloy, written as [7]:

$$\lambda = a \cdot \lambda_{111} + (1-a) \cdot \lambda_{100} \quad (3)$$

where λ_{111} and λ_{100} are spontaneous magnetostriction coefficients of a polycrystalline alloy. The theoretical value of a coefficient for an isotropic alloy is 0.60, which is similar to the a value in the 0-3 composite due to the embedded alloy particles dispersed randomly in the epoxy matrix. As for the 1-3 composite containing the particles with EMD ⟨1 1 1⟩, the value of a should be larger than 0.60 because the ⟨1 1 1⟩-textured particles are aligned along the rod direction, parallel to the measuring magnetic field. It is known that λ_{111} is larger than λ_{100} in RFe_2 Laves-phase compounds [1, 10]. Therefore, it is reasonable that the λ_a-enhancement effect is achieved for the 1-3 type $Tb_{0.25}Ho_{0.65}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ composite compared with the 0-3 type one, which can be attributed to its embedded particles of EMD ⟨1 1 1⟩ and the larger λ_{111}. The value of $I_{(222)}/I_{(311)}$ decreases with increasing V_f, indicating the lowering of the alignment degree along ⟨1 1 1⟩ accordingly, which would lead to the decrease of the coefficient a. As can be seen in Fig. 5, λ_a decreases when V_f exceeds 30 vol.%, which can be explained by equation 3. Thus, to obtain the 1-3 type particulate composites with good magnetostrictive properties, the alloy particle content of 30 vol.% is optimum.

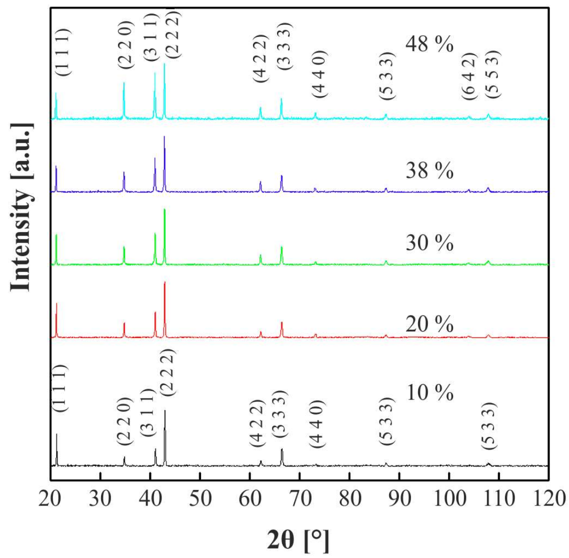

Fig. 6. XRD patterns of the 1-3 type $Tb_{0.25}Ho_{0.65}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ composites with various particle volume fraction.

In order to further understand the impact of magnetic anisotropy and magnetization nature on the magnetostrictive properties of the composites, the longitudinal magnetization $M_{\parallel}$ (the measuring field direction parallel to the particles alignment) was measured. As an example, the curves $M_{\parallel}/M_{max}$ = f(H) and $\lambda_{\parallel}/\lambda_{max}$ = f(H) for the $Tb_{0.25}Ho_{0.65}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ composite have been plotted in Fig. 7, where λ_{max} and M_{max}

denote $\lambda_{\|}$ and $M_{\|}$ in the maximum field of 10 kOe, respectively. It is obvious that the $M_{\|}/M_{max}$ curve for 1-3 type composite lies above the one of 0-3 type, indicating the easy saturation for magnetization, attributed to EMD ⟨1 1 1⟩ particles lying along the measuring field. In addition, the $\lambda_{\|}/\lambda_{max}$ curve reveals the similar tendency, showing that the 1-3 type composite has a good low-field magnetostrictive properties, e.g. $\lambda_a \sim 430$ ppm/3 kOe.

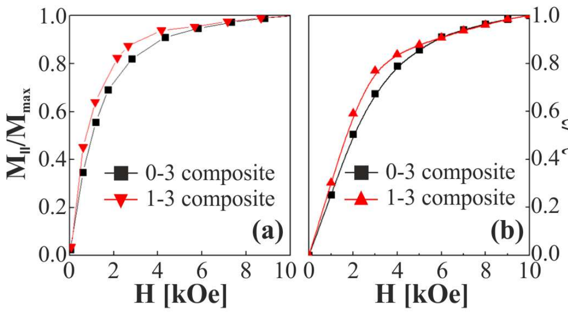

Fig. 7. Magnetic field dependence of (a) normalized magnetization $M_{\|}/M_{max}$ and (b) normalized magnetostriction $\lambda_{\|}/\lambda_{max}$ for the $Tb_{0.25}Ho_{0.65}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ composites.

4. Conclusions

Magnetostrictive $Tb_xHo_{0.9-x}Nd_{0.1}(Fe_{0.8}Co_{0.2})_{1.93}$ ($0 \leqslant x \leqslant 0.40$) alloys and their composites were prepared. The easy magnetization direction (EMD), magnetostriction, magnetization, and macroscopic structure in the composites have been investigated by means of XRD, VSM and a standard strain technique. The magnetic anisotropy compensation point was found to be around $x = 0.25$. For this composition, the EMD at room temperature was lying along the ⟨1 1 1⟩ axis. The magnetic curing field made the particles align as a particulate chain and also caused the particles rotating along their EMD direction. Particle volume fraction V_f is an important factor that affects magnetostrictive properties, and the optimal V_f chosen in this study, was of about 30 vol.%. The ⟨1 1 1⟩ preferred oriented pseudo 1-3 type composite was successfully fabricated by embedding and aligning particles in a passive epoxy matrix in the presence of an oriented magnetic field of 12 kOe. An enhanced magnetoelastic effect and large low-field magnetostriction $\lambda_a \sim 430$ ppm/3 kOe, was obtained for the rod sample of $x = 0.25$, which was of 72 % value of its polycrystalline alloy although it only contained 30 vol.% alloy particles. This enhanced effect can be attributed to the larger λ_{111} (as compared to λ_{100}), low magnetic anisotropy, EMD along the ⟨1 1 1⟩ axis, the ⟨1 1 1⟩-textured orientation and chain-like structure. The good magnetoelastic properties, in spite of the fact that the composite contained only 30 vol.% alloy particles with light rare-earth Nd element in the insulating epoxy, would make it a promising magnetostrictive material system. In addition, this work provides an epoxy-resin bonding route in preparing magnetostrictive composites.

Acknowledgements

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