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Simultaneous deposition of Ni nanoparticles and wires on a tubular halloysite template: A novel metallized ceramic microstructure

Yubin Fu[a,b,*], Lide Zhang[a]

[a]Institute of Solid State Physics, China Academy of Sciences, Hefei 230031, China
[b]Luoyang Ship Material Research Institute, Luoyang 471039, China

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Abstract

Tubular halloysite can be used as a template to fabricate a novel metallized ceramic microstructure through electroless plating. Reduction of Pd ions by methanol is conducted to initiate Ni plating. There is a simultaneous deposition of Ni nanoparticles on the outer surface and discontinuous wires in the lumen site of the halloysite template obtained. The different deposition could be caused by the different composition distribution of ferric oxide impurity in the wall due to the isomorphic substitution during the formation of halloysite template. Its magnetic property is mainly attributed to the Ni nanoparticles, not the wires. The metallized ceramic microstructure has the potential to be utilized as a novel magnetic material.

Keywords: Halloysite template; Electroless deposition; Ni nanoparticles and wires; Ceramic microstructure; Composite

1. Introduction

The properties of a material strongly depend on its micro- and nanostructure. Metallic nanoparticles or wires, for example, have the potentially useful electronic, magnetic, and catalytic properties deriving from their nanoscopic size and shape. One important problem in obtaining the desired properties of a material, however, is the controlled synthesis of mono-dispersed nanoparticles or wires on a defined surface, and their assembly into one-, two- and three-dimensional microstructures. One possible approach to realizing such structures is to utilize a template-directed synthetic technique [1]. Artificial templates, such as carbon nanotubes [2], ordered arrays of alumina [3], and porous polymer membranes [4], have been used to create arrangements of nanocluster or wires. Biological templates, such as lipids [5], DNA [6], protein S-layers [7] and microtubules [8], have also been used to conduct the nucleation, deposition and assembly of inorganic nanoparticles. Up to now, these studies have mainly been focused on the artificial and biomolecular templates, and few researches have been done on a tubular halloysite template that occurs naturally in clay.

The halloysite template (composition: $Al_2Si_2O_5(OH)_4$ H_2O 1:1 layer aluminosilicate), a super-fine clay material, often occurs as an ultramicroscopic hollow tubule with a multi-layer wall in nature [9]. Clays are widely used as a precursor in the manufacture of conventional and advanced ceramics and as fillers in organic composites such as resins, rubbers, and plastics. Surface modification of the super-fine clays by chemical methods could be useful in altering the particle–particle or particle–matrix interactions, and improving the overall performances of ceramic composites [10]. Some studies on the surface modification of halloysite have been conducted by an adsorption of the multi-layer charged organic macromolecules to fabricate a nanofilm [11]. Halloysite can also be used as a template for metallic Ni film or nanoparticles for the fabrication of a metallized composite to modify its dielectric or magnetic properties [12,13]. However, we have not found any studies, in which metallic nanoparticles and wires are simultaneously deposited on the halloysite template.

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[*] Corresponding author. Luoyang Ship Material Research Institute, Luoyang 471039, China. Fax: 86 379 64913642.
E-mail address: ffyybb725@vip.sina.com (Y. Fu).

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In the paper, a simultaneous deposition of Ni nanoparticles on the outer surface and wires in the cavity of the halloysite template is obtained through an electroless plating. To perform the electroless plating, it is necessary to activate the halloysite template. The conventional catalyst is a colloidal Sn–Pd acid solution; however, this not only requires a complicated treatment process, but its strong acidity can also destroy the clay substrate. In the paper, the in situ reduction of Pd ions by methanol on the surface of the halloysite was conducted to initiate the electroless deposition of nickel [14].

Furthermore, the magnetic property of the as-plated or post-annealed Ni on the template is investigated when the template is oriented in the resin and aligned with each other under an applied magnetic field.

2. Experimental section

2.1. Fabrication of the metallized ceramic microstructure

Firstly, the white halloysite powder (trade name Premium halloysite from New Zealand China Ltd.) was activated by Pd for the initiation of the electroless deposition as described in the literature [14]: 5 mg of sodium tetrachloride palladate (Na_2PdCl_4, Fluka) was dissolved in 50 mL of methanol containing a small amount of polyvinyl pyrrolidone (PVP), and then 50 mg of halloysite after dispersed ultrasonically in methanol solution for 10 min was added. The solution mixture was then continuously stirred for 5 h at room temperature, and an in situ reduction reaction of Pd ion by methanol occurred [14]. The reduction reaction can be expressed as follows:

$$PdCl_4^{2-} + CH_3OH \underset{\text{Template}}{\overset{\text{Halloysite}}{\longrightarrow}} Pd^0 + HCHO + 2H^+ + 4Cl^-. \qquad (1)$$

Finally, the supernatant was removed by a centrifugation method, and the precipitation was washed several times with water to remove the excess Pd ions and methanol, and freeze-dried, and then for electroless plating.

Second, a plating bath was primarily composed of nickel sulfate, borane dimethylamine complex (DMAB, Fluka), and EDTA · 4Na [15]. The plating bath was diluted into a 10% concentration solution for use and degassed for about 10 min by using helium gas. Fifty milligrams of the activated halloysite powder was added to 50 mL of the 10% plating bath, and the mixture was stirred continuously. At room temperature, the mixture immediately turned black, and hydrogen bubbles began to form. The electroless deposition reaction of Ni can be expressed as follows:

$$\begin{aligned} &3Ni^{2+} + 3(CH_3)_2NHBH_3 + 6H_2O \\ &\quad \underset{Pd}{\longrightarrow} 3Ni^0 + B + 3(CH_3)2NH_2^+ + 2B(OH)_3 \\ &\qquad + 9/2H_2 + 3H^+. \end{aligned} \qquad (2)$$

The plating reaction was continued with stirring to keep the halloysite particles well dispersed until the evolution of hydrogen gradually decreased, and a black metallized particle began to settle on the bottom. After plating, the supernatant bath was eliminated by the centrifugation, and the black sample was washed with a large amount of water to remove the residual plating salts. The metallized sample was freeze-dried and transferred to a film-coated Cu grid for TEM examinations.

The metallized sample was put into a stove with a vacuum of 1×10^{-3} Pa, which was heated up to 673 K, and held for 1 h, and then cooled in furnace down to room temperature.

2.2. Microscopic examinations

Halloysite template and metallized sample were transferred on a film-coated Cu grid and observed under a field emission scanning electron microscopy (FESEM, Hitachi S-4300, Japan) and transmission electron microscopy (TEM, JEOL JEM2010, Japan), respectively. All samples were firstly adhered on a double-faced conductive glue, and then sputtered in a vacuum with a thin layer of Pt to increase their conductivity for the SEM observation. A selected area electronic diffraction pattern (SADP) was recorded to examine the crystal structure of Ni nanoparticles. X-ray diffraction (XRD) was performed by an X-Pert diffractometer (Philips, Holland) with an accelerative voltage of 40 kV, a current of 40 mA, a Cu $K\alpha$ radiation, and a graphite monochromater at a scanning speed 2.4°/min.

In a chemical analysis, Ni on halloysite was brought into a solution by treating the composite with a diluted nitric acid, and then determined by an atomic absorption spectroscopy (Hitachi 180-80). Element of B in Ni was quantitatively determined by an X-ray photoelectron spectroscopy (XPS, Axis Ultra, Kratos Analytic Ltd., UK).

In order to examine the deposition feature of Ni in the inner cavity of halloysite, the metallized sample was embedded in an epoxy resin (cured for 48 h at 333 K) to prepare an ultra-thin section for the TEM examination.

2.3. Determination of its magnetic property

The values of inherent coercive force (iHc), saturated magnetization (Ms), and residual magnetization (Mr) were determined at room temperature by a vibrating sample magnetometer (VSM, LDJ-9500, American) and magnetic balance (AB204-N). The maximum magnetic field applied was 1.0 T, and the magnetic hysteresis loops were not corrected by a demagnetization treatment. The determination values were calculated by the weight of Ni in the metallized samples.

In order to determine the effect of the template alignment on the magnetic property of Ni, the post-annealed sample was uniformly dispersed into an epoxy resin, and then put into a hollow cylinder model with a diameter of 5 mm and height of 7 mm. The cylinder model was positioned into an applied magnetic field (3–4 T) to make the template be aligned with each other during the curing of the resin matrix. The aligned cylinder was also used to determine its iHc, Ms, and Mr with a magnetic field applied in a parallel or perpendicular direction to the template alignment as illustrated in Fig. 1. A bulk Ni powder, the post-annealed and as-plated samples randomly dispersed in resin, were also determined for a comparison.

The aligned cylinder (Fig. 1) was also used to directly prepare the ultra-thin section for the TEM examination.

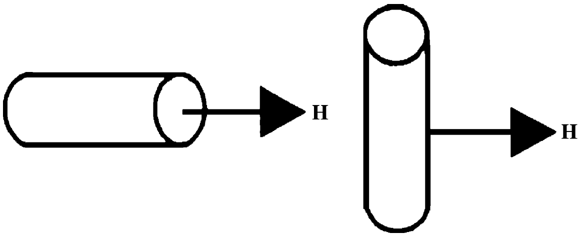

Fig. 1. Sketch map of the alignment samples under the magnetic field applied with the parallel (left) or perpendicular (right) directions, respectively, to determine its property. (H means the applied magnetic field direction.)

3. Results and discussions

The microscopic examinations show that the white halloysite powder has a short cylindrical shape (Fig. 2a), and a clearly hollow tubular structure (arrow, Fig. 2b). The halloysite template has an average length of 1–2 μm, a diameter in the range of 75–150 nm, and an average pore diameter of 15 nm. After plating, the halloysite turns black, and Ni nanoparticles are uniformly deposited on its surface (Fig. 2c and d). Statistical results based on 500 counts show that the diameter of the nanoparticles is primarily in the range of 20–30 nm, approximately 75–80% of the total. The results also indicate that after post-annealed at 673 K, the deposition features of Ni nanoparticles and the shape of halloysite template remain unchanged.

The chemical analysis shows that the composite contains about 30–35 wt% Ni, and the XPS analysis indicates the Ni nanoparticles contain a small amount of element B, which is attributed to the reducing agent DMAB in the plating bath. The XRD results indicate that the as-plated Ni is in an amorphous state, and the amorphous structure has got something to do with the content of element B in Ni [16] (Fig. 3b). After post-annealed, it becomes an fcc (face-centered cubic) crystal structure (Fig. 3c), which can be

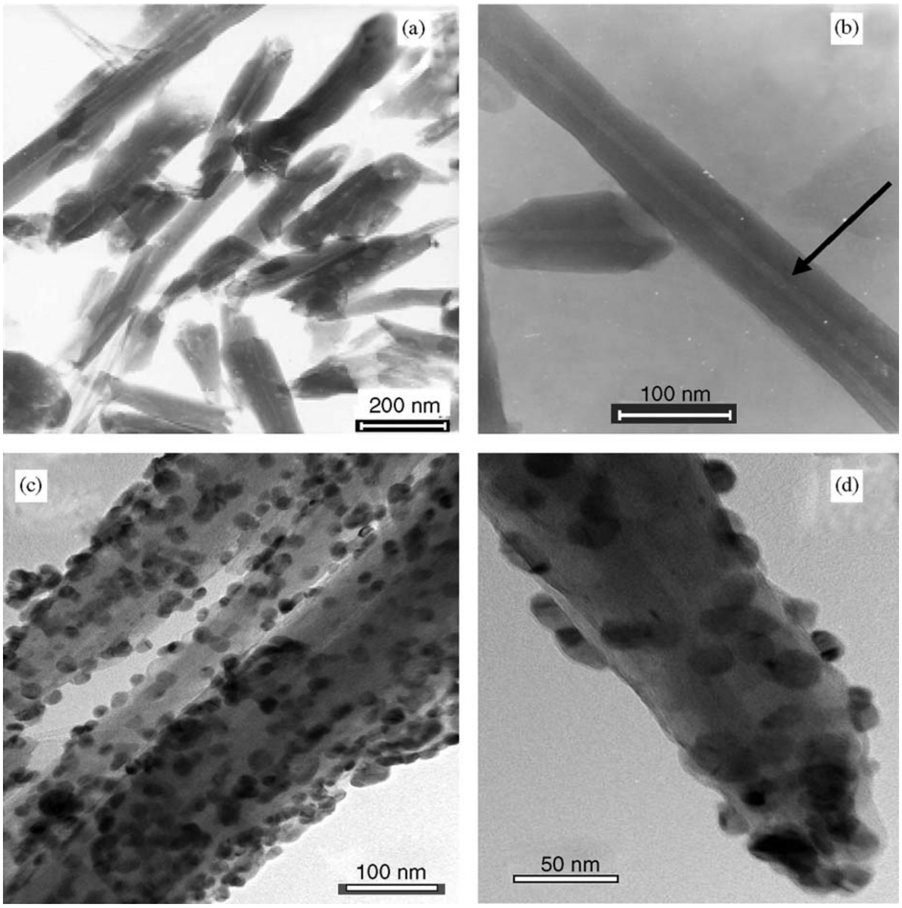

Fig. 2. TEM images of (a) the cylinder shape, (b) the hollow tubular structure of halloysite (arrow). (c) and (d) TEM and SEM images of Ni nanoparticles on the outer surface of halloysite template.

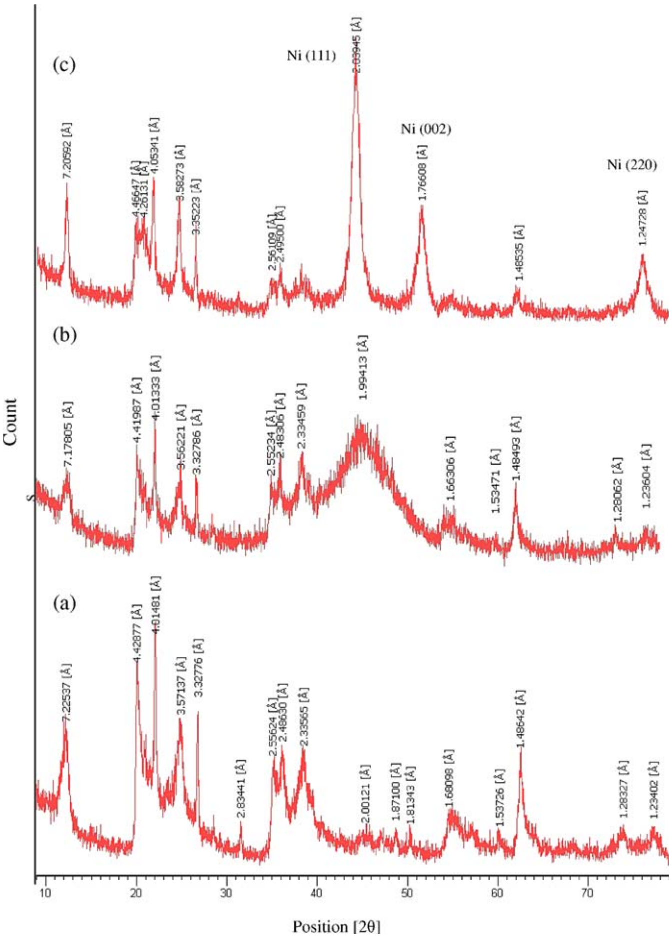

Fig. 3. XRD patterns of (a) halloysite template, (b) the as-plated and (c) the post-annealed samples at 673 K.

confirmed by the clear diffraction rings of Ni in the SADP images (Fig. 4).

Metallic nickel is simultaneously deposited in the cavity of tubular halloysite (Fig. 5). Fig. 5a shows that there is a black wire-like structure (called wire for short in the paper) inside the tubular halloysite with a length of 700 nm, a diameter of 15 nm, and an aspect ratio of approximately 47 (arrows). Fig. 5b is the cross-section images of a metallized halloysite, and in its tubular central core, it seems to have a porous or puffy structure. The porous structure could be caused by the slow liberation of hydrogen from the inner cavity in the plating process. Fig. 5c shows a longitudinal section along the tubule axis, in which there are two discontinuous Ni wires with a length of 40 nm and a diameter of approximately 15 nm. The diameter of the discontinuous Ni wires is primarily consistent with the average pore diameter of the tubule. The result in Fig. 5d directly confirms the Ni wire inside the halloysite is a discontinuous nanowire (arrow).

Hence, it can be concluded that the discontinuous Ni wires are formed in the lumen cavity of the halloysite template. However, because of the thick tubular wall and the uniform deposition of Ni nanoparticles on the halloysite surface, the Ni wires cannot be observed in many cases. Therefore, it is difficult to provide how high the yield of Ni wires is.

However, why do the Ni nanoparticles deposit on the outer surface and wires simultaneously in the cavity of the halloysite?

An experimental comparison was made to compare with the literature [14]. In the literature, the Pd-activated halloysite was firstly dispersed in water, and then mixed with plating bath in an equal volume. The result shows that

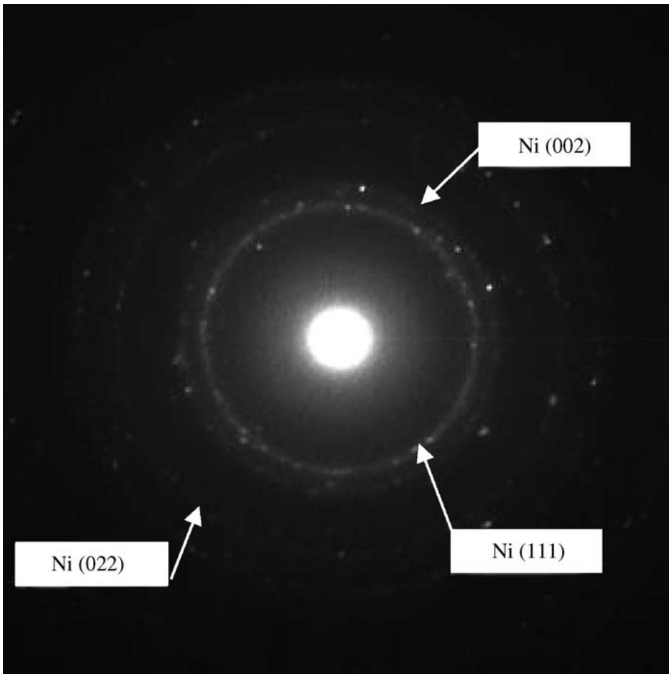

Fig. 4. SADP image of Ni on halloysite template after post-annealed at 673 K.

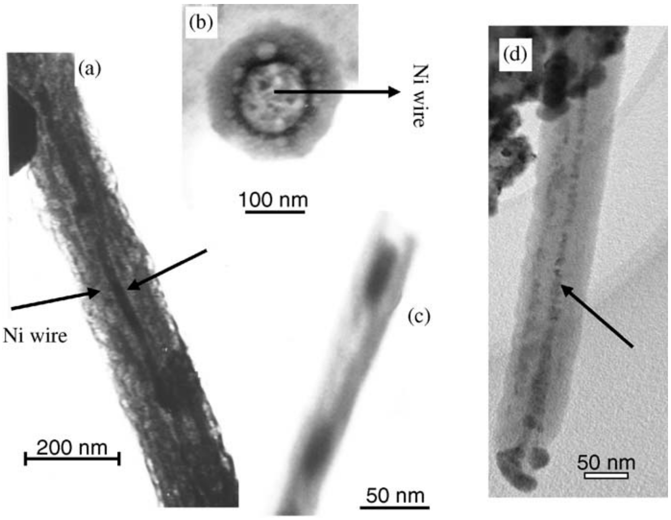

Fig. 5. (a) Formation of a Ni wire inside the tubular halloysite (arrows). (b) Cross section of a Ni wire, and its porous structure. (c) Longitudinal section of the discontinuous Ni wires in the cavity of halloysite. (d) Discontinuous wire in the template (arrow).

it is difficult to form Ni wire in halloysite, and there are very few wires observed. In this case, the pre-existence of water inside halloysite before plating would make the plating bath difficult to diffuse into its lumen site. In the current paper, the Pd-activated halloysite was freeze-dried into powder, and then mixed with plating bath. The result indicates that there is the Ni wire formed in halloysite. In this case, in plating, the capillary force can drive the plating bath into inner side of halloysite to deposit and form Ni wires. The formation of the discontinuous Ni wire would be due to the incomplete removal of gas or the slow exchange of plating bath in the lumen site of halloysite in plating.

On the other hand, the chemical analysis indicates that halloysite contains a small amount of metal oxides, such as the impurity of 0.25% Fe_2O_3. Some studies have shown that the driving force for halloysite curling up to form a tubular structure from a plate kaolinite is due to an isomorphic substitution of Si(IV) by Al(III) or Fe(III) [17,18], and the isomorphic substitution will result in a different composition in the outermost and inner surface of the central core. In a very approximate way, we can associate the chemical properties of the halloysite tubule's outermost surface with the properties of SiO_2 and the properties of the inner cylindrical core with Al_2O_3 [11]. It would also be reasonable to assume that the impurity of Fe_2O_3, like Al_2O_3, could have a different distribution in the wall of the halloysite due to the isomorphic substitution.

The relatively higher amount of Fe_2O_3 in the inner surface of the central core could have more activated points or sites to initiate a greater reduction of Pd, and eventually to initiate a greater deposition to form a Ni wire; however, the smaller amount of Fe_2O_3 on the outer surface would cause a smaller degree of Pd reduction, resulting in the separate Ni nanoparticles on the halloysite. Line-scan EDS composition analysis on a single halloysite cylinder proved that Fe is discretely distributed on its outer surface, which is consistent with the discrete distribution of Pd and Ni nanoparticles [13,14].

TEM examination also indicates that the cylindrical halloysite templates are oriented in a resin matrix by the magnetic alignment, and they are parallel to each other in most cases (arrow, Fig. 6a). The cross sections of the alignment templates are mainly circular, not an oval shape (Fig. 6b). This would indirectly confirm that the templates are parallel; because if the templates are randomly dispersed in the resin matrix, they will cause the microtome knife to cut with a tilt angle to their axis of the templates, there would be some oval cross-section images obtained.

Therefore, it can be concluded that in electroless plating, Ni nanoparticles and wires can simultaneously be deposited on the halloysite template to form a microstructure. This is a novel metallized ceramic microstructure, as illustrated in Fig. 7.

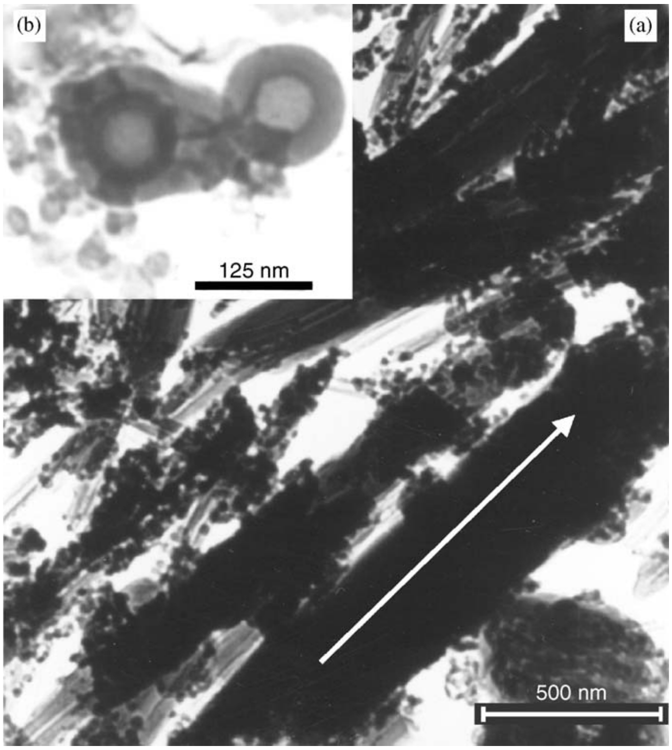

Fig. 6. TEM examination of the magnetic alignment of template in the resin (a), and arrow indicates the orientation direction. (b) Two parallel cylinder templates with Ni deposited in the inner tubules with a circular cross section.

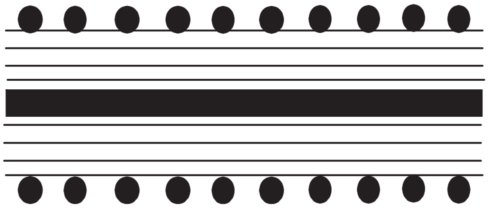

Fig. 7. Sketch map of the novel metallized ceramic microstructure.

The values of iHc, Ms, and Mr of the metallized samples are presented in Table 1. Because the magnetic property of halloysite template can be negligible, it is reasonable to think that the magnetic properties are primarily attributed to metallic Ni. From Table 1, it can be seen that after post-annealed at 673 K, the values of iHc, Ms and Mr increase much higher than that of the as-plated and the bulk Ni. The huge difference would be attributed to the sum contributions of a magneto-crystalline anisotropy and single domain effect, as described in the literature [13].

However, from the comparison of aligned samples with the randomly dispersed sample in Table 1, it can be seen that the magnetic alignment has no great effect on its magnetic property. On one hand, the magnetic property would be primarily caused by the magneto-crystalline anisotropy and single domain effect of Ni nanoparticles. On the other hand, because the average diameter of the Ni wires is roughly 15 nm, far smaller than the size of a single magnetic domain of Ni (20–40 nm) [19,20], it could make the Ni wires be in a super-paramagnetic state, and cause

Table 1
Comparison of their magnetic properties of the metallized samples after the post-annealing treatment and magnetic alignment

Samples	Parallel[a]	Perpendicular[a]	Random[a]	Bulk Ni	As-plated
IHc (Oe)	246.8	237.5	253.6	100	7.38
Ms (emu/g)	48.86	51.91	57.37	55	2.26
Mr (emu/g)	19.46	17.52	21.46	2.7	0.04

Parallel or perpendicular means the magnetic field was applied in a parallel or perpendicular to the alignment direction of the samples, respectively, as described in Fig. 1. Random means the sample was uniformly dispersed in resin without alignment, seen in Ref. [13].

[a] Indicates the metallized sample was post-annealed at 673 K.

the Ni wires have no contribution to the magnetic property. Hence, there is no such a big difference in the magnetic property between the aligned and randomly dispersed samples.

In summary, a novel metallized ceramic microstructure is fabricated through a simultaneous deposition of Ni nanoparticles and wires on a tubular halloysite template in the electroless plating. Different metals or alloys (such as Co, Fe) can also be deposited on halloysite template to prepare an interesting material for its low weight, low cost, and high magnetic property.

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