Material design and shape memory properties of smart composites composed of polymer and ferromagnetic shape memory alloy particles

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Abstract

Ferromagnetic shape memory alloys (FSMAs) such as NiMnGa are expected to be new practical actuator materials with high driving frequency by magnetic field and large strain due to the shape memory effect (SME). However, the brittleness and poor workability of FSMAs, especially at a polycrystalline state, are serious problems and should be improved for a practical use. From this viewpoint a smart composite has been designed by a combination of a polymer matrix and FSMA particles (FSMAP), and a systematic investigation has been done for a NiMnGa-FSMAP/epoxy smart composite. This paper summarizes the design concept and some experimental results of the smart composite. It is pointed out that the single-crystal NiMnGa-FSMAP are easily made by mechanical crush due to the brittleness of FSMAs, and microstructural control is also possible by applying magnetic field during curing. Experimental study revealed that the NiMnGa-FSMAP/epoxy smart composites exhibit both tensile ductility and SME, and that shape memory properties become improved by decreasing particle size of FSMAP. It is concluded that the FSMAP/polymer smart composite has a large potential to be a new practical actuator material.

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1. Introduction

Shape memory alloys (SMAs) exhibiting a shape memory effect (SME) and/or superelasticity (SE) are important smart materials with sensing and actuating functions. SME stands for a shape recovery at a critical temperature during heating, thus SMAs sense temperature. SE stands for a shape recovery at a critical stress during unloading, thus SMAs also sense force. Both SME and SE are the phenomena related with thermoelastic martensitic transformation, and the shape recoverable strain depends on crystallographic difference between parent and martensite phases. It is known that SMAs exhibit the highest work per volume ( = force × strain/volume) of actuator materials [1]. It is also known that, although a large number of SMAs have been reported, only Ti–Ni SMA is practically and industrially used. Other SMAs than Ti–Ni have some problems such as insufficient SME, poor mechanical properties, brittleness, poor corrosion resistance and poor biocompatibility.

Even for the Ti–Ni practical SMA some problems are also pointed out [2]. A problem is a limited actuation temperature below 400 K. Higher actuation temperature is required for chemical plants and engine applications. Then, our group has investigated high-temperature SMAs such as Ti–Ni–Pt exhibiting high martensitic transformation temperature up to 1300 K [3–6]. Second problem is a possibility of Ni-hypersensitivity due to constituent Ni atoms of Ti–Ni. SMAs are widely required for advanced biomedical applications such as SE stents and SE guide-wires, but the practical applications are limited especially for implantation in Europe due to the constituent Ni. For the biomedical applications our group has systematically developed new Ni-free biomedical SMAs composed of Ti and nontoxic elements [7–11]. SE achieved at present exceeds 5% for a Ti–Nb–Al SMA. Third problem is a limited frequency in motion around 100–200 Hz in comparison with 108 Hz for piezoelectric materials such

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PZT [1]. The reason of low frequency is that the speed of motion is limited by heat transfer since heating and cooling cycles are required for the appearance of SME.

From the viewpoint of quick motion, ferromagnetic shape memory alloys (FSMAs) such as NiMnGa and Fe–Pd are fascinating in which the actuation can be caused by applying magnetic field. A problem of FSMAs is that quite large magnetic filed is required for inducing martensitic phase transformation. It is not practical to use a superconducting magnet for actuation. Then, instead of martensitic phase transformation, actuation due to reorientation of martensite variants is practically available since small magnetic field generated by a conventional electric magnet is enough for actuation. In this case, the shape recoverable strain is similar to that obtained by martensitic transformation but the shape recovery force is small (around a few MPa). Another problem of most FSMAs is the brittleness and poor difficulty in shaping and forming, especially at the polycrystalline state. Single crystal FSMAs are relatively ductile, thus, single crystal FSMAs are generally used for investigations. However, single crystals are costly and shaping is still a problem.

According to the background, we have proposed a smart composite composed of a polymer matrix and ferromagnetic SMA particles (FSMAP) for a shape memory material with quick motion [12,13]. The polymer matrix enhances the ductility and FSMAP play a role of actuating component. In this paper, the polymer/FSMAP smart composites are focused, and the material design and experimental results obtained for NiMnGa-FSMAP are presented.

2. Material design

It is well known that wire-shape SMAs are one of effective reinforcements to improve tensile strength and ductility of metal-matrix composites due to the large shape recovery force of SMAs against applied force [14–17]. In the fabrication process of these SMA-base composites, prestrained SMA wires are embedded during forming. Some problems of the wire-embedded composites are shaping and forming after synthesis. The composites with complex shape are difficult to be fabricated in this case.

In terms of shaping and forming, isotropic composites containing SMA particles (SMAP) are advantageous. Kobayashi and co-workers reported Al matrix composite containing Ti–Ni SMA particles and found good mechanical properties [18]. A schematic fabrication process of SMAP/polymer composites is drawn in Fig. 1(a), and it is clear that the composite is isotropic because of randomly distributed SMAP. It should be mentioned that single-crystal FSMAP can be easily fabricated by crushing mechanically due to the brittleness of FSMAs if the particle size becomes smaller than the grain size. Moreover, it is also easy to fabricate anisotropic composites and fabrication method is drawn in Fig. 1(b). Since FSMAP are ferromagnetic, they are preferentially distributed by applying magnetic field due to the easy axis of magnetization of crystals. Such anisotropic composites are similar to single crystal FSMA, but the fabrication of composites is much easy with low cost in comparison with conventional method for making single crystals. In this paper, however, only the isotropic composites fabricated without magnetic field are focused for the experimental data.

3. Experimental procedure

FSMA selected was NiMnGa. Three chemical compositions of NiMnGa were used to be 51Ni-26Mn-23 mol%Ga (51Ni26Mn23Ga) and 54Ni-21Mn-25 mol%Ga.
(54Ni26Mn23Ga) and 51.5Ni-23.5Mn-25 mol%Ga (named 51.5Ni23.5Mn25Ga). 51NiMnGa and 54NiMnGa were designed to be the martensite phase at RT, and 51.5Ni23.5Mn25Ga was designed to be the parent phase at RT, by considering the relationship between the martensitic transformation temperature ($M_s$) and the electron atom ratio (e/a) [19,20]. The alloys were made by arc melting method with W electrode in Ar-1%H$_2$ using high purity elements of 99.99%Ni, 99.9%Mn and 99.999%Ga. The alloys were homogenized at 1273 K for 3.6 ks in vacuum followed by an ordering treatment at 1073 K for 3.6 ks in vacuum [21]. Then, the alloys were crushed mechanically with various grain sizes from 25 to 150 μm followed by annealing at 1073 K for 900 s. The powder fabricated was observed by a scanning electron microscope (SEM) to identify the morphology of the powder. Differential scanning calorimetry (DSC) was performed with a heating/cooling rate of 10 K/min in Ar using Shimadzu DSC-60. DSC was used for both FSMAP and smart composites.

The smart composites were fabricated by mixing NiMnGa SMAP with epoxy matrix. The epoxy used was composed of a base of epoxy resin (Epikote 828) and a curing agent (Tohmide 280-B). The volume fractions of SMAP were changed from 0 to 50%. The smart composites were mixed and cured at 353 K under the pressure of 10 MPa for the duration from 130 to 173 ks. Then, specimens for mechanical tests were made by cut and the damaged surface was removed by polishing. It should be noted that no difference in mechanical properties was detected for the smart composites depending on curing time. Tensile tests and constant stress test during thermal cycles were performed by Shimadzu SG-3961-1 and Netzsch DMA (dynamic mechanical analyzer) 242C. The gaze sizes of plate-shape samples were 0.9 x 5 x 22 mm$^3$ for tensile tests and 1 x 4 x 10 mm$^3$ for DMA. DMA was carried out in a temperature range from 263 to 323 K. The heating/cooling rate of DMA measurement was 5 K/min and frequency was 1 Hz. A static force and a dynamic force were selected from 1 to 8N.

4. Results and discussions

4.1. Transformation temperatures

Fig. 2 shows a SEM micrograph of 51Ni26Mn23Ga FSMAP with particle size less than 150 μm [12]. Forward martensitic transformation start temperature $M_s$, forward martensitic transformation finish temperature $M_f$, reverse martensitic transformation start temperature $A_s$ and reverse martensitic transformation finish temperature $A_f$ are listed in Table 1. It was clear that austenite transformation finish temperature ($A_f$) is higher than RT for 51Ni23Mn26Ga and 54Ni21Mn25Ga, and that $A_f$ is lower than RT for 51.5Ni23.5Mn25Ga. The major apparent phases of both for 51Ni23Mn26Ga and 54Ni21Mn25Ga are the martensite phases at RT, and that for 51.5Ni23.5Mn25Ga is the parent phase at RT. These phase constitutions were also identified by the XRD analysis. It was also found that martensitic transformation temperatures of the smart composites are similar to those of SMAP themselves. This indicates that the existence of the polymer matrix does not influence the martensitic transformation temperature of SMAP. Therefore, the change of the transformation temperatures is not necessarily taken into account for the FSMAP/epoxy smart composites.

4.2. Tensile properties

Fig. 3 shows the stress–strain curves of the 51Ni26Mn23Ga-FSMAP/epoxy smart composites containing 0–20 vol% FSMAP. These SS curves were obtained by tensile tests at RT. It was found that the epoxy (which does not contain FSMAP) exhibits the largest elongation over 100% and the lowest yield stress around 1.8 MPa. With increasing the volume fraction of FSMAP, both yield stress and ultimate tensile strength (UTS) exhibits a tendency to increase but the elongation decreases in general manner. It should be mentioned that the 20 vol%–FSMAP/epoxy composite shows both low strength and low fracture strain even though the composite contains the largest FSMAP fraction in this figure. It should be also mentioned that the tensile strength and elongation obtained by tensile tests largely scatter when the volume fraction of FSMAP...
increases over 20%. Such scatters must be caused by interfacial problem and/or defects (pore) introduced during curing treatment.

4.3. Shape memory properties evaluated by stress–strain curves

Fig. 4 shows a part of cyclic stress–strain curve of the 50 vol%-51Ni26Mn23Ga-FSMAP/epoxy smart composite tested at 288 K. The arrows in the figure indicate shape recovery by heating over $A_f$, and the arrows correspond to the shape recovery strain. The particle size of FSMAP is 75–150 μm. It is found that the yield stress of the composite is about 3 MPa, and that shape recovery occurs by heating. The low yield stress may be due to low flow stress of epoxy polymer and/or low stress for reorientation of martensite variants in NiMnGa [22]. The shape recovery strain seems to increase with increasing the number of deformation cycles, and reaches 1.7% after sixth cycle. It is clear that the smart composite exhibits a good SME in tensile deformation due to the existence of the epoxy matrix. It is noted no tensile deformability appears for polycrystalline NiMnGa. However, the specimen was degraded after seventh cycle.

4.4. Shape memory properties evaluated by strain-temperature curves

In order to clarify the shape recovery behavior of the smart composites, constant stress tests during thermal cycles were carried out. Fig. 6 shows the strain-temperature curves of the epoxy and 10 vol%-54Ni21Mn25Ga-FSMAP/epoxy smart composite during heating. These curves were obtained by DMA where the static force and the dynamic force were 2 and 1N, respectively. It was found that creep deformation appears near and above RT: the creep deformation of these materials is caused by softening of

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**Table 1**

Martensitic transformation temperatures of NiMnGa FSMAP

| FSMAP         | Forward martensitic transformation finish temperature, $M_f$(K) | Forward martensitic transformation start temperature, $M_s$(K) | Reverse martensitic transformation start temperature, $A_s$(K) | Reverse martensitic transformation finish temperature, $A_f$(K) |
|---------------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|
| 51Ni26Mn23Ga  | 252                                                           | 273                                                           | 293                                                           | 308                                                           |
| 54Ni21Mn25Ga  | 267                                                           | 302                                                           | 281                                                           | 314                                                           |
| 51.5Ni23.5Mn25Ga | 232                                                           | 247                                                           | 251                                                           | 261                                                           |

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Fig. 5 shows the relationship between shape recovery strain by heating and applied stress evaluated using Fig. 4. Although some scatters are seen in the data, the shape recovery strain seems to be proportion to the applied stress: 0.4%/MPa. This indicates that the rearrangement of martensite variants progresses proportionally to the applied stress in the composites due to the elastic backstress of the epoxy matrix. The lowest stress required for SME is estimated to be 1 MPa, and that stands for the minimum stress for reorientation martensite variants.

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**Fig. 4.** Partial cyclic stress-strain curves of FSMAP/epoxy smart composite containing 50 vol%-51Ni26Mn23Ga-FSMAP. Note that the numbers shown in the figure stand for the number of cyclic deformation, and that arrows indicate shape recovery by heating. The cycles from 1st to 3rd are removed in this figure for the simplicity [13].

**Fig. 5.** Stress–strain curves of 51Ni26Mn23Ga FSMAP/epoxy smart composites.
polymer. High temperature polymers should be used as matrix materials if shape recovery above RT is desired.

In order to evaluate shape recovery of the smart composites containing 51Ni26Mn23Ga FSMAP, the following thermal cyclic tests were performed. Firstly, the smart composite was cooled down to 280 K (below $M_s$) and deformed at martensite state. After the deformation, the deformed specimen was heated up to 323 K (higher than $A_s$) under the tensile stress of 0.1 MPa. If the composites possess a SME, shape recovery should be observed. The tensile stress of 0.1 MPa was required to keep straight shape of specimens. Then, finally, the specimen was cooled down to 280 K under the same tensile stress being less than 0.1 MPa. Since no shape change is expected during cooling, the negative shape change after the thermal cycle is due to the shape recovery, and the strain in shape change in this case is the shape recovery strain.

Fig. 7 shows the results of the thermal cycle tests using the 50 vol%-51Ni26Mn23Ga-FSMAP/epoxy smart composite. Note that the specimens were deformed at 280 K by the stresses shown in the figure, unloaded down to 0.1 MPa, heated up to 323 K and then cooled down to 280 K under the constant tensile stress of 0.1 MPa. Creep deformation was seen above 310 K, and shape recovery was recognized near the reverse transformation temperatures listed in Table 1.

Fig. 6. Creep strain observed for a constant stress test during heating by DMA. Note that the static force was 2N, the dynamic force was 1N and FSMAP was 51Ni26Mn23Ga. Softening is seen above 295 K for the epoxy and above 305 K for the smart composite.
were used for measuring strain-temperature curves. Fig. 8 (a–c) are strain-temperature curves of 51.5Ni23.5Mn25Ga FSMAP/epoxy composites with different particle sizes: (a) 75–150 μm, (b) 25–75 and (c) 0–25 μm. The dynamic and static forces were selected to be 5.2 MPa, approximately. It was found that no creep deformation was observed in these figures, and that shape change appears regardless of particle size. However, the transformation strain becomes larger with decreasing particle size of FSMAP. Transformation strain of 0.4% was achieved. Optical microscopic observation revealed that several pores were introduced in the specimens during fabrication, and that the size of pores was comparable to that of FSMAP. Then, samples with larger FSMAP contain larger pores. Such microstructural inhomogeneity must reduce mechanical properties. Although the details of effects of particle size on mechanical properties are not sufficiently understood, these pores and defects introduced during fabrication must reduce SME of the composites.

5. Summary

For the development of ferromagnetic shape memory alloys (FSMAs), a new smart composite composed of polymer matrix and FSMA particles (FSMAP) are proposed in this paper. The polymer matrix enhances the ductility, and shape memory properties appear by FSMAP. The material design and shape memory behavior of the NiMnGa-FSMAP/epoxy smart composite were described. Since NiMnGa SMA is brittle, the fabrication of SMAP and the smart composite is easy in this case. The transformation temperatures of the smart composites are similar to those of FSMAP; therefore, a change of transformation temperatures during processing is not necessarily to be taken into account. However, the shape memory properties are much influenced by the creep deformation of the matrix, internal defects, the volume fraction and the size of FSMAP. The maximum shape recovery strain at present time is around 2% for tensile stress–strain tests and 0.4% for the constant stress tests during thermal cycles. It is concluded that the SMAP/polymer smart composites are hopeful as new shape memory materials, but that the improvement of shape memory properties is required for practical applications.

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