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Fabrication of Shape Memory Alloy Powder/Polymer Smart Composites

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Shape memory alloys (SMAs) such as Ti-Ni are effective reinforcement of composites, because SMAs can generate large shape recovery force and strain. Since these SMA-reinforced composites are generally strengthened by prestrained SMA wires or fibers, the anisotropy of mechanical properties must appear due to one directional fiber reinforcement. This anisotropy leads to inconvenience in shaping and forming of the composites. Therefore, in order to improve the formability of SMA composites, polymer matrix composites containing shape memory alloy powder (SMAP) with random orientations have been proposed and developed in this study. Besides, the fundamental mechanical characteristics of the SMAP/polymer composites were investigated. Two kinds of SMAs, *i.e.*, TiNiCu and NiMnGa, were prepared, pulverized into powders, and mixed with epoxy matrix. The smart composites fabricated were supplied for tensile tests, and the results obtained were discussed in comparison with epoxy composites containing pure cupper powder which does not exhibit shape memory effect. It was found that the SMAP/epoxy smart composites exhibited large elongation around 10-40%, and that the yield stress of the smart composites increased with increasing volume fraction of SMAP. Besides, the yield stress of smart composites was higher for TiNiCu SMAP than that for NiMnGa SMAP. The difference in yield stress of these two SMAP/epoxy composites must come from the difference in stress for reorientation of martensite variants.

Key words: shape memory alloy, smart composite, polymer, NiMnGa, TiNiCu, epoxy, mechanical properties

1. INTRODUCTION

It is well known that shape memory alloys (SMAs) are one of effective reinforcements to improve tensile strength and ductility of Al-base, Ti-base and polymer-base composites due to the large shape recovery force of SMA which resists against applied force [1-4]. In the fabrication process of the SMA-base composites, SMA wires are usually used which are prestrained during forming the composites. Then, internal stress against applied tensile stress is generated in the SMA base composites. The internal stress generated by SMA wires reduces the effective applied tensile stress, thus the apparent tensile properties are improved in the composites [1].

A drawback of these SMA-wire composites is disability of forming and shaping after the synthesis of composites. This is because the anisotropy of mechanical properties must appear due to the one directional strengthening by wires. Besides, the strengthening caused by residual stress due to SMA wires easily changes by forming and shaping. By taking the shaping and forming after synthesis into account, isotropic composites are advantageous as compared with anisotropic composites. If such isotropic composites are obtained, a large number of shaping method can be utilized such as the injection molding method.

Based on the background, SMA powder (SMAP) is advantageous instead of SMA wire for the isotropic characteristics of smart composites. The principle of fabrication is drawn in Figure 1. The SMAP used here is deformed during mechanical crushing to introduce prestrain, and the prestrained SMAP is distributed randomly in matrix. Then, isotropic shape recovery stress is generated around SMAP as internal stress, resulting strengthening of the smart composites. Although a similar method was proposed by Kobayashi and co-workers and applied for SMAP reinforced Ti matrix composites by plasma spark sintering, Ti-Ni SMAP produced by gas atomizing method was not prestrained before synthesis [5]. On the other hand, prestrained SMAP is easily produced by mechanical crushing from SMA ingots with low cost and it should be emphasized that most SMAs are brittle except for Ti-Ni and titanium base SMAs. In this paper, the fabrication of SMAP/epoxy smart composites and tensile mechanical properties of the composites were studied.

2. EXPERIMENTAL PROCEDURE

SMAs used in this study were selected to be TiNiCu SMA and NiMnGa SMA. TiNiCu SMA exhibits comparable shape memory effect and lower ductility than Ti-Ni binary alloy [6], supposing that this SMA has advantageous in powder fabrication. NiMnGa is now strongly paid attention to be a new high performance ferromagnetic SMA driven by magnetic field [7-9]. NiMnGa SMA is also suitable for the purpose of this study, since NiMnGa is brittle. Besides, cupper powder was used as a reference.

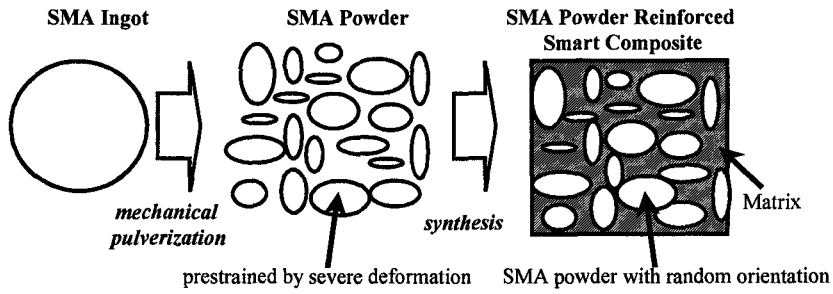

Figure 1 The fabrication of shape memory alloy powder (SMAP) reinforced smart composites.

TiNiCu SMA of 50mol%Ti-40mol%Ni-10mol%Cu was supplied as a rapidly solidified ribbon. The details of ribbon fabrication were described in Ref.[10]. The TiNiCu powder was fabricated by mechanical crushing, and a heat treatment at 1073K for 3.6ks was carried out for the appearance of shape memory effect [10]. NiMnGa SMA of 54mol%Ni-21mol%Mn-25mol%Ga as made by arc melting method with W electronode in Ar-1%H_2 using 99.99%Ni, 99.9%Mn and 99.999%Ga. NiMnGa alloy was homogenized at 1273K for 3.6ks in vacuum followed by an ordering treatment at 1073K for 3.6ks [11]. NiMnGa was also crushed mechanically. It is noted that, though the mechanical properties of the composites must depend on the prestrain and defects of SMAP, experimental evaluation of prestrain and defects was not carried out. The powder size of both powders was less than 150μm. Differential scanning calorimetry (DSC) was performed to clarify the martensitic transformation temperatures with a heating/cooling rate of 10K/min and Ar atmosphere. Besides, the magnetic transition (Curie) temperature of NiMnGa powder was evaluated using thermogravimetry (TG) with a magnetic field. Commercial Cu powder used was 99.9% purity and the size was 75μm approximately. No heat treatment was done for the Cu powder.

The smart composites were fabricated by mixing either NiMnGa or TiNiCu with epoxy matrix. The reference composites were made by mixing Cu powder with epoxy matrix. The epoxy used in this study was composed of a base of epoxy resin (Epikote 828) and a curing agent (Tohmide 280-B). The volume fractions of powders were changed from 0%, 5%, 10% and 20% for NiMnGa and Cu powders, and 10% only for TiNiCu powder, since the amount of TiNiCu SMAP obtained was insufficient. The compositions of specimens were listed in Table 1. The smart composites were mixed and cured at 353K under the pressure of 10MPa for the duration from 130ks to 173ks. Then, the specimens for mechanical tests were made by cut and the damaged surface was removed by polishing. The size of tensile specimens was 2mm in thickness, 5mm in width and 50mm in length. It should be noted that no difference in mechanical properties was detected depending on curing time. Tensile tests were performed at room temperature (RT: 295±2K) with the strain rate of $5x10^{-4}$/s using Shimadzu Autograph 100NI.

Table 1 Volume fractions of Cu powder and SMAPs of epoxy-base composites fabricated.

Powder	Volume fraction of powder, V (%)			
	0	5	10	20
Cu	○	○	○	○
NiMnGa	–	○	○	○
TiNiCu	–	–	○	–

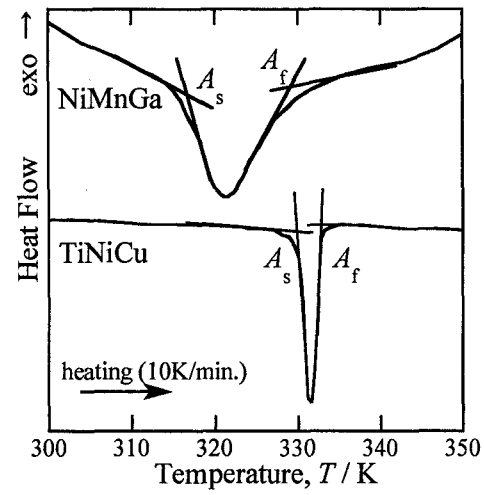

Figure 2 DSC heating curves of NiMnGa and TiNiCu SMA powders.

Table 2 Martensitic transformation temperatures of NiMnGa and TiNiCu SMAPs.

SMA	M_s / K	M_f / K	A_s / K	A_f / K
NiMnGa	-	-	316	331
TiNiCu	320	316	331	335

M_s: martensitic transformation start temperature
M_f: martensitic transformation finish temperature
A_s: austenite transformation start temperature
A_f: austenite transformation finish temperature

3. RESULTS AND DISCUSSIONS

3.1 Transformation Temperatures

Martensitic transformation temperatures (M_s) were determined by DSC. Figure 2 shows DSC heating curves of NiMnGa and TiNiCu SMAPs. The transformation temperatures evaluated from DSC are listed in Table 2. It was found that austenite transformation temperatures (A_s and A_f) of both SMAPs were higher than RT. However, the martensitic transformation start and finish temperatures (M_s and M_f) of NiMnGa SMAP were not clearly determined. This is because the temperature range of the TG-DSC used for NiMnGa is above RT and M_s and M_f of NiMnGa SMAP

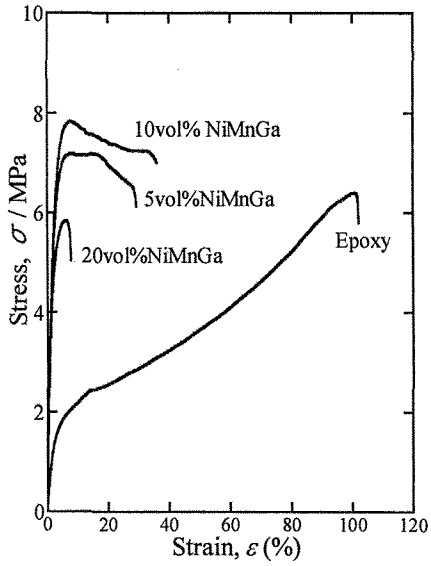

Figure 3 Stress-strain curves of NiMnGa/epoxy composites containing 0 (epoxy), 5, 10 and 20vol%NiMnGa SMAP.

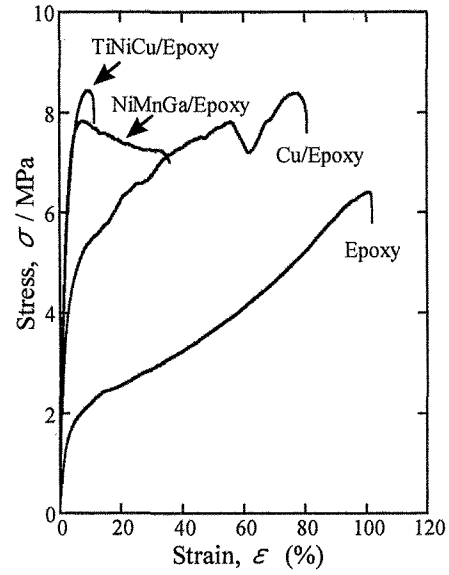

Figure 4 Stress-strain curves of epoxy and and composites containing 10vol%Cu, 10vol%NiMnGa and 10vol%TiNiCu.

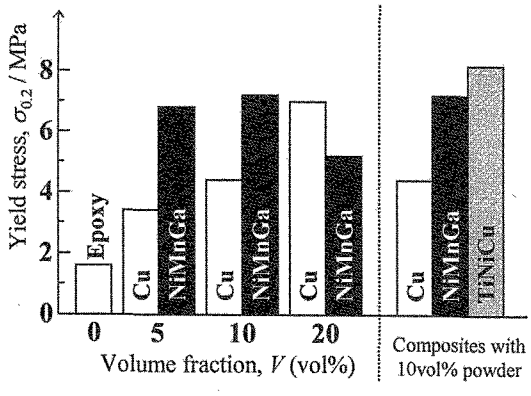

Figure 5 Comparison of yield stress of the composites. The left side shows the yield stress vs. volume fraction of Cu and NiMnGa powders, and the right side shows yield stress of the composites containing 10vol%Cu, 10vol%NiMnGa and 10vol%TiNiCu powders.

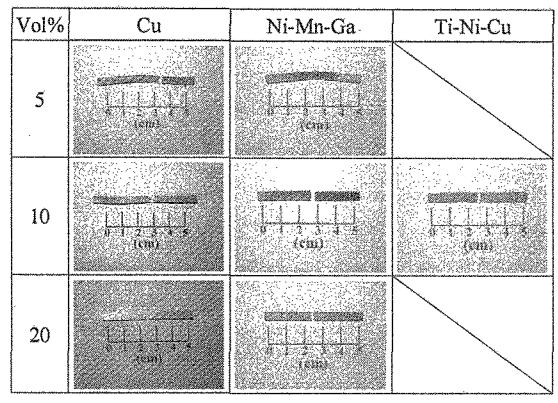

Figure 6 Macroscopic shapes of the composites after fracture.

are estimated near RT. In this case, quantitative determination could not be done because the cooling rate could not be kept constant near RT and heat flow depends on cooling rate. TG curves obtained with a magnetic field suggested that the Curie temperature of the NiMnGa SMAP is 375K.

3.2 Tensile properties

Figure 3 shows the stress-strain curves of NiMnGa-SMAP/epoxy smart composites with various volume fractions of the SMAP. It was found that the epoxy (which does not contain SMAP) exhibits the largest elongation over 100% and the lowest yield stress around 1.8MPa. With increasing the volume fraction of NiMnGa SMAP, both yield stress and ultimate tensile strength (UTS) increase but the elongation decreases, except for the 20vol%NiMnGa/epoxy smart composites. The opposite dependences of elongation and strength on reinforcement fraction are generally seen in most composites. Then, it can be said for the NiMnGa SMAP/epoxy smart composites that the SMAP raises strength but reduces elongation in general manner. It should be mentioned that the 20vol%NiMnGa/epoxy composite shows low strength and fracture strain even though the composite contains the largest fraction of SMAP. The brittleness of the 20vol%NiMnGa/epoxy composite must be an interfacial matter.

Figure 4 shows the stress-strain curves of the epoxy and the composites containing 10vol% powders of TiNiCu, NiMnGa and Cu. The elongation decreases and strength increases by adding the powders regardless of kind of powders. The details will be discussed.

3.3 Effect of shape memory alloy powder (SMAP)

As shown in Figs. 3 and 4, it is clear that yield stress and UTS of the composites are improved by adding Cu, NiMnGa and TiNiCu powders. Figure 5 shows the comparison of yield stress of the composites. By comparing composites containing Cu and NiMnGa powders, the yield stress is higher in composites containing SMAP than in the composites containing Cu powders, except for the 20vol%SMAP composite. Therefore, SMAPs introduced are effective reinforcement, at least when the amount of addition is less than 20vol%.

By comparing TiNiCu and NiMnGa shown in the right side of Fig.5, the strength is slightly higher for the TiNiCu/epoxy composites than that for the NiMnGa/epoxy composite. This can be explained that the stress for reorientation of martensite variants is higher in TiNiCu (50-300MPa for Ti-Ni SMA [6]) than in NiMnGa (a few MPa [12]). Then, SMA exhibiting higher reorientation stress of martensite variants may more effective to improve strength.

The reversible strain of SMAs due to the reorientation of martensite variants reaches a few or several per cent in many cases. From this point of view, the elongation of SMAP/epoxy composites must be enough large associated with reorientation of martensite variants. Figure 6 shows the macroscopic shapes of tensile specimens after fracture. Facture occurred after homogeneous deformation in all specimens. As shown in Figs.3, 4 and 6, the fracture strains obtained were relatively large values around 10-40% for the SMA/epoxy composites. However, Cu/epoxy composites exhibit comparable or larger elongation than SMAP/epoxy composites. Since the Cu powder used was 99.9%purity, the Cu powder must be soft and exhibit larger elongation than the SMAPs. Besides, the size and shape of powders must be an important factor to influence mechanical properties of these composites. The size of Cu powder is smaller (~75μm) than that of SMAs (<150μm). Thus, in order to develop mechanical properties of SMAP/epoxy smart composites, the effects of powder size, shape and distribution of SMAPs should be revealed and controlled.

4. CONCLUSIONS

(1) Shape memory alloy powder (SMAP) reinforced polymer matrix smart composites with isotropic physical properties were proposed and some examples of the SMAP/epoxy smart composites were successfully fabricated.

(2) The smart composite containing 10vol%NiMnGa SMAP exhibited good mechanical properties such as high strength over 7MPa in yield stress and large elongation over 35%.

(3) The yield stress of SMAP/epoxy smart composites increased with increasing volume fraction of SMAP, and the yield stress of the smart composites was higher than those of the epoxy and Cu/epoxy composites.

(4) The SMA/epoxy composites exhibited high elongation around 10-40%. The elongation was comparable or slightly lower than that of Cu/epoxy composites.

(5) 20vol%NiMnGa SMAP/epoxy composite exhibited lower ductility and strength than 10vol%NiMnGa SMAP/epoxy composite. The fracture of these composites must be affected by the size and morphology of reinforcement, for example.

(6) TiNiCu SMAP/epoxy smart composites showed high yield stress but low elongation in compassion with NiMnGa SMAP/epoxy smart composites. The difference in yield stress must be due to the difference in stress for reorientation of martensite variants between TiNiCu and NiMnGa.

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