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A composite functional material with shape memory effect exhibiting a giant reversible straining

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A new design principle of a composite functional material on the basis of a material with shape memory effect has been proposed and tested in experiment. This design can be applied to the majority of traditional materials with shape memory effect (ferromagnetic and non-ferromagnetic alloys as well as for polymers) and it provides in all cases a giant reversible straining though the "one-way" shape memory effect is used only. This design is especially promising for applications in the fields of micro- and nano-electromechanical systems.

Предложена и экспериментально испытана новая схема композитного функционального материала на основе материала с эффектом памяти формы. Эта схема может быть применена для большинства традиционных материалов с памятью формы — ферромагнитных и неферромагнитных сплавов, а также полимеров. Во всех случаях она обеспечивает гигантскую обратимую деформацию, хотя используется только "односторонний эффект памяти формы". Эта схема особенно перспективна для применений в области микро- и наномеханики.

Recently, a great attention is given to the development and studies of novel functional materials, in particular, those changing the shape or dimensions as a response to action of an external field, e.g., temperature, magnetic, or electric one. Such materials are of great importance, especially in designing of micro- and nano-electromechanical systems (MEMS and NEMS, respectively), because the conventional mechanical schemes are unsuitable in the field of small dimensions.

In numerous works, the bimorphous layered structures made of different materials are used to provide an elastic strain of an actuator as a response to action of heat, electric, or magnetic field [1–3]. Various physical effects are used for the straining: inverse piezoelectricity, thermal expansion, magnetostriction, etc. For example, in [4], the bimorphous structures based on films of NiTi alloy with shape memory effect (SME) sputtered onto silicon substrates have been studied and the reversible bending strains ε of a bimorphous actuator have been demonstrated to be controllable by the heating action of the current running through the structure. Unfortunately, all such structures exhibit only a relatively small controllable bend due to a small layer length change as a response to an external field ($\varepsilon = \Delta l/l$ not exceeding 0.1 %).

A wide variety of shapes can be given to the metal alloys with SME, such as springs, shells, etc., the active element shape can be varied arbitrarily (twisted, bent, stretched, etc.). The reversibility of such variations, however, is attained only using a special process ("training") that is hardly suitable in engineering. Moreover, the strain in such a "double-way" SME is as a rule at least one decimal order smaller than in the "one-way" one.

In this work, a new design principle is proposed for a composite based on a SME material providing a much more considerable bend straining as compared to the known functional materials. Moreover, the SME is maintained in microscopic alloy samples [6]. This is a prerequisite for solution of a practical task of great importance, namely, for development of micro- and nanometer size scale actuators. Such actuators might be applied in MEMS, NEMS, tools for embryology, micro- and nanosurgery, etc. The goals to be attained are as follows: (1) to propose a novel design for a composite functional material based on an alloy with SME providing a considerable reversible straining using only the "one-way" shape memory of the alloy; (2) to prepare and study in experiment a functional material based on the rapid-quenched $Ti_{50}Ni_{25}Cu_{25}$ alloy using gluing and electroplating and modeling of actuators controlled by thermal field and electric current; (3) to estimate theoretically the maximum strains and forces attainable in the layered structures with SME.

Fig. 1 presents schematically the composite explaining its principle of operation. The composite includes a SME layer (*1*), e.g., a rapid-quenched ribbon or film of a SME alloy; the later is connected rigidly with an elastic layer of a usual metal (*2*). A novel feature in the preparation of such a bimetal plate is the fact that the SME ribbon is subjected to a pseudo-plastic tensile prestraining prior to connection with the elastic element. It this case, the reversible bend of the composite under cyclic change of temperature or magnetic field (if the SME alloy is ferromagnetic [7]) may exceed by several orders of magnitude that of an

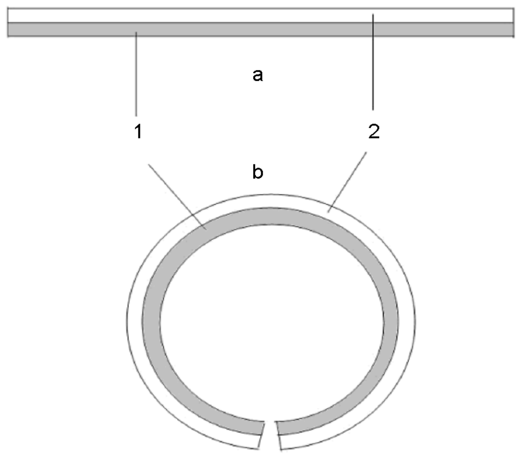

Fig. 1. Schematic view of a bimorphous element consisting of a SME layer (1) and elastic layer (*2*) in martensitic (a) and austenitic (b) state of the SME layer.

usual bimetal plate and by at least one order that of the alloy with double-way shape memory. The use of such a prestressed composite with SME provides new functional potentials for the actuator and a quantitative enhancement of the known application schemes.

The operation principle of the composite is based on the fact that the flexural strain of the composite plate includes compression at the inner side and tension on the outer one. The straining reversibility can be explained as follows. Under a rather high external stress, the temperature of the structure martensitic transition (austenite-martensite) rises [5]. In a stressed sample, the martensite is generated when it is cooled from the austenitic state and passes the martensitic phase transition point. That generation will start first within the maximum strassed regions. The correspondingly oriented versions of martensite will arise mainly (stretched or compressed along the tension or compression axes). That is what is refferred to as the pseudo-plastic or reversible strain. If a homogeneously pseudo-plastically stretched element with SME in the martensitic state is connected rigidly with an elastic layer and then heated above the point of the inverse martensitic transition, then the martensite transits into austenite and a high stress arises that compresses the SME layer. The elastic layer is strained less, so the composite becomes bent strongly. The pseudo-plastic tension measure may exceed several per cent. The bend value is limited in practice by the strength properties of the elastic layer but not by those of the SME one. If the bent composite is cooled down under the martensitic transition temperature, then the elastic layer being returning into the unstressed state will stretch the SME one pseudo-plastically into the martensitic state again, so the composite will be straightened.

The one-way SME results usually in a single shape recovery in spite of the repeated periodic heating, that is why it is referred to under its name. An actuator made of the SME composite will change periodically its shape under periodic cooling and heating. It is seen that the concept itself of the composite actuator design is realizable using any known SME material, either ferromagnetic or non-ferromagnetic alloy or polymer [8]. In this work, the ribbons of $Ti_{50}Ni_{25}Cu_{25}$ alloy prepared by rapid quenching of the melt were used to study the composite design principle in experiment. The material has been developed in 90s for application in temperature sensors, because it is practically feasible and the martensitic transition therein is observed near room temperature [9]. However, the rapid-quenched alloys are under intense study to date and numerous works are devoted thereto (see, e.g., recent publications [10–14]). The interest is due to the fact that the ribbons are often rapidly quenched into amorphous state, the crystalline structure being recovered therein under annealing. The amorphous state exhibits no SME. The alloy properties are changed abruptly during the recrystallization and it takes the ability to the martensitic transition and thermomechanical memory effects. Thus, the alloy mentioned is a convenient object to study the relationship between the structure and functional thermomechanical properties.

The preparation of a composite comprising a $Ti_{50}Ni_{25}Cu_{25}$ ribbon includes three stages, namely, the ribbon annealing, its pseudo-plastic stretching, and the composite making by connection with an elastic metal layer. In this work, two techniques have been used to apply the elastic layer, namely, the amorphous ribbon gluing and electrolytic deposition of a nickel layer. The 30–40 μm thick ribbons were prepared by cooling rapidly the initial melt of nearly stoichiometric $Ti_{50}Ni_{25}Cu_{25}$ composition on a rotating copper drum. The rapid cooling (at a rate of about 10^6 K/s) results in formation of amorphous structure in the ribbon. By annealing the ribbon in an oxidizing gas medium (air) at 500°C for 7 min as was described in [10], a micro-crystalline ribbon

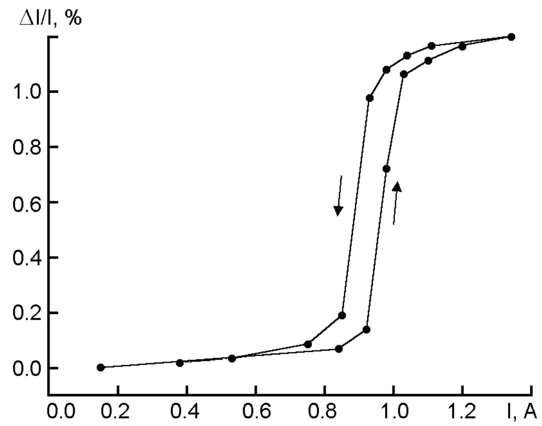

Fig. 2. Relative length change of a $Ti_{50}Ni_{25}Cu_{25}$ ribbon as a function of current strength.

structure was obtained that was confirmed by electron microscopy. The ribbon so made exhibits the SME.

At the second stage, the $Ti_{50}Ni_{25}Cu_{25}$ ribbon was subjected to pseudo-plastic stretching. The ribbon was loaded by a force of 3 to 30 N. Then a current about 1 A was passed through the ribbon. The Joules heat had heated the ribbon above the inverse martensitic transition temperature, A_f. Then the current was switched off and the ribbon was elongated by about 1–3 % when being cooled down under the complete martensitic transition temperature, M_f. The initial ribbon length was recovered as the current was switched on again. The ribbon strain was measured using an optical microscope. A representative plot of the ribbon relative length variation vs the current strength under 10 N loading is shown in Fig. 2. A hysteresis typical of SME alloys is observed within the intermediate state region about the martensitic transition.

To prepare the composite material by "gluing", the $Ti_{50}Ni_{25}Cu_{25}$ ribbon pre-stretched as described above as well as an amorphous steel ribbon prepared by rapid quenching, too, were connected together by a standard technique using an ethyl cyanoacrylate adhesive. To prepare the composite material by "deposition", the $Ti_{50}Ni_{25}Cu_{25}$ ribbon was coated on one side with electrolytically deposited nickel layer. The deposition technique was developed basing on that described in GOST 9.305-84. Arrangements were made to provide the electrolytic coating at a temperature lower than the martensitic transition onset point.

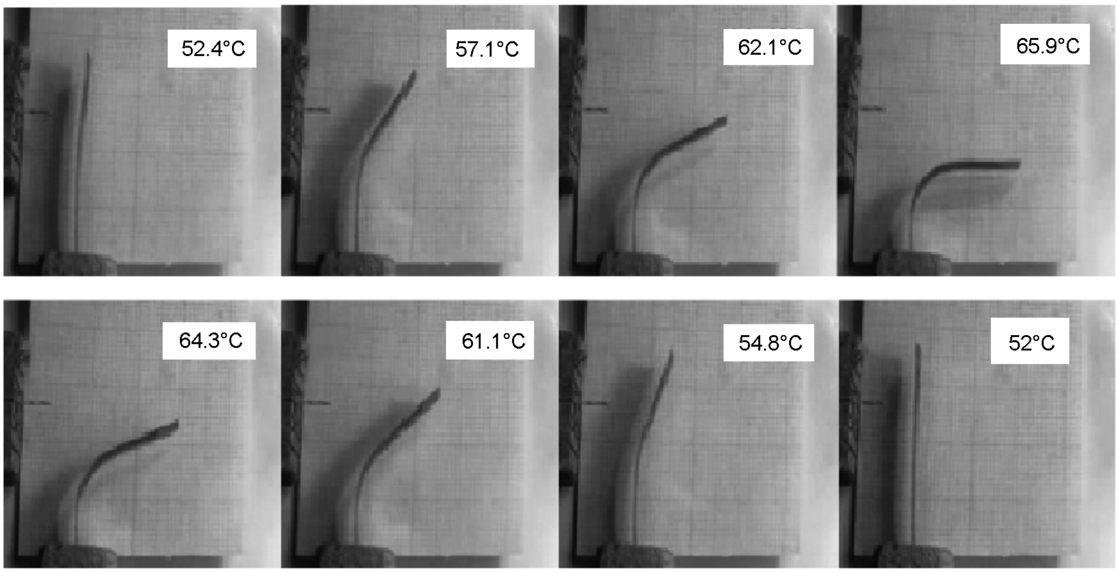

Fig. 3. An experiment on the reversible flexural strain of a glued composite under thermocycling.

The nickel layer thickness can be varied within wide limits. In the prepared composite experimental samples, the SME layer and elastic one had approximately equal thickness.

In the experiment intended to study the composite properties, the glued sample was placed in a thermostat provided with a transparent cover. The sample was fixed above a squared paper sheet so that its flexural strain could be observed from above. A heating element was arranged under the sample. The temperature was measured using a copper/constantan thermocouple. The sample was heated and cooled slowly within the temperature range of 50 to 70°C, that is, within the martensitic transition region of the $Ti_{50}Ni_{25}Cu_{25}$ alloy. The shape variations of the composite actuator sample was recorded using a camcoder. Then the bent actuator image was quantized. The surface curvature was determined from coordinates of three points in the maximum bend region. The flexural strain was calculated as

$$\varepsilon = \frac{h}{2R}, \quad (1)$$

where ε is the dimensionless strain value; h, the composite thickness; R the curvature radius at the maximum bend point (at the sample middle).

The experimental results for the reversible flexural straining of a composite sample under thermocycling in a homogeneous temperature field are illustrated by a series

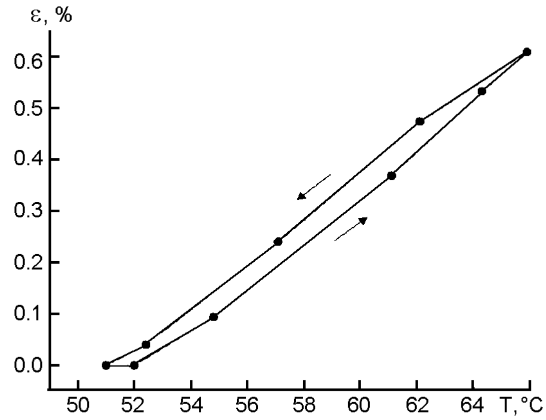

Fig. 4. The temperature dependence of the flexural strain of a composite.

of images in Fig. 3. A giant reversible flexural strain of the composite is observed exceeding 90°. The temperature (T) dependence of the flexural strain is plotted in Fig. 4. The hysteresis in that plot differs from the abrupt and wide hysteresis of the ribbon strain (see Fig. 2). This is due most likely to the continuously varying stresses in the connection region between two composite layers (the stress being increasing under compression and decreasing under straightening). As a result, the hysteresis is more diffuse. The material linear strain at the maximum bend point calculated using (1) is ε = 0.65 %.

Fig. 5 illustrates an experiment on repeated reversible flexural straining of the composite material prepared by electrolytic deposition of Ni onto one side of a rapid-

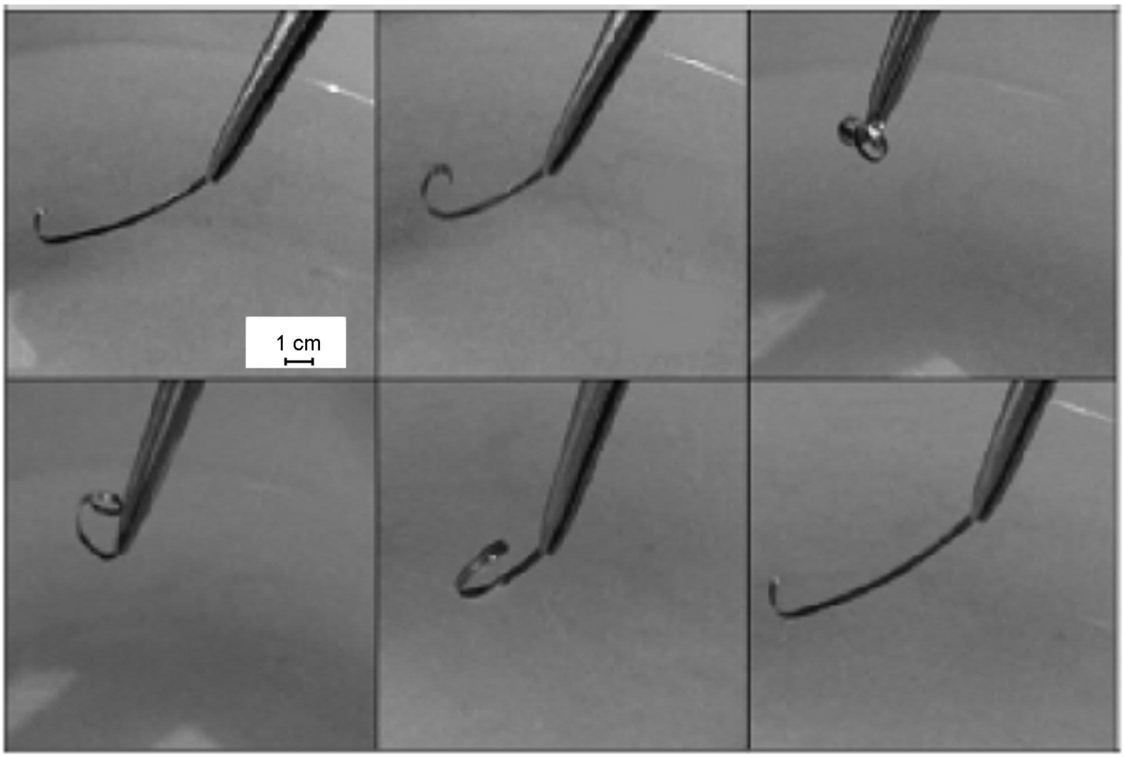

Fig. 5. An experiment on the reversible flexural strain of a composite prepared by electrolytic Ni deposition onto rapid-quenched $Ti_{50}Ni_{25}Cu_{25}$ ribbon.

quenched $Ti_{50}Ni_{25}Cu_{25}$ ribbon under heating↔cooling. The composites were heated and cooled slowly within the temperature range of 50 to 70°C, that is, within the martensitic transition region of the $Ti_{50}Ni_{25}Cu_{25}$ alloy. As a result, a strong repeated reversible flexural strain was observed up to about 1 % (according to (1)), i.e., exceeding 720°.

To describe theoretically the giant flexural strains of the bimorphous SME composite, a simplified mathematical model was constructed. In this initial stage of investigation, the model does not take into account the martensitic phase transition and hysteresis features in the temperature dependence of the composite curvature. As a first approximation, only the initial state (the SME layer in the martensitic state) and the final one (austenitic SME layer) are considered.

When flexural strains are absent (the composite being blocked between rigid planes), only the compression strain takes place at heating. The compression value δ in the course of shape recovery can be get from the minimization condition of the composite elastic energy W:

$$W = \frac{E_1 \cdot (\Delta l - \delta)^2}{2 \cdot l_0^2} \cdot h_1 \cdot b \cdot l + \frac{E_2 \cdot \delta^2}{2 \cdot (l_0 + \Delta l)^2} \cdot h_2 \cdot b \cdot l. \quad (2)$$

In (2), E_1, E_2 denote the first order elasticity moduli of the SME layer and elastic one, respectively; h_1, h_2, thickness of the SME layer and elastic one, respectively; Δl, the SME layer elongation under pseudo-plastic straining; l_0, the initial SME layer length (prior to pseudo-plastic straining); b, the composite width; l, the composite length in the austenitic state. The result ($\Delta l/l_0$ <<1) as a first approximation)is get as

$$\delta = \frac{E_1 \cdot h_1 \cdot \Delta l}{E_1 h_1 + E_2 h_2}. \quad (3)$$

As the composite transits into austenitic state, a bending moment arises therein. The straight shape is maintained because that moment is compensated by the reaction force moment of the support. According to the 3rd law of mechanics, the support reaction force is equal to the force generated by the composite. Let the latter be estimated. To that end, let the equilibrium equation be derived for the composite with one half fixed and a force preventing the bending applied to the free end. According to the equilibrium equation, the force can be described as

$$F = \frac{M}{l}, \tag{4}$$

where F is the force to be sought; M, the bending moment; l, the arm (the sample length from the fixation point to the free end).

The internal bending moment is calculated as

$$M = \frac{E_1 \cdot h_1^2 \cdot b \cdot (\Delta l - \delta)}{2 \cdot l_0} + \frac{E_2 \cdot h_2^2 \cdot b \cdot \delta}{2 \cdot l_0}. \tag{5}$$

Substituting (5) into (4) and assuming the equal thickness and elasticity moduli of both layers ($E_1 = E_2 = E,\ h_1 = h_2 = h$), we get for the force

$$F = \frac{E \cdot h^2 \cdot b \cdot \Delta l}{2 \cdot l \cdot l_0}. \tag{6}$$

To get an expression for the curvature of composite being in the free state, let us assume that the Bernulli-Euler beam bend theory is valid for the case and the composite layers are absolutely equal in length to one another. Under such assumptions, the internal bending moment can be supposed to be constant over the length, thus, the composite surface will be a cylindrical one. The Bernulli-Euler beam bend theory supposes a small strain $\Delta l/l_0 <<1$ but does not require a small apex angle at bending. Then, within the frames of that theory, the elastic energy W should be minimized to determine the surface curvature radius R and the apex angle α of the composite:

$$W_{\sum}(\alpha,R) = \frac{b}{2l_0} \cdot E_1 \cdot \int_{R}^{R+h_1} [l_0 - \alpha(R+x)]^2 dx + \frac{b}{2l_0} \cdot E_2 \cdot \int_{R+h_1}^{R+h_2+h_1} [l_0 + \Delta l - \alpha(R + h_1 + y)]^2 dy, \tag{7}$$

x and y being the integration parameters.

Then, let us solve the system of equations:

$$\frac{\partial W_{\Sigma}(\alpha,R)}{\partial \alpha} = 0, \quad \frac{\partial W_{\Sigma}(\alpha,R)}{\partial R} = 0. \tag{8}$$

The solution is a rather complex expression, therefore, a partial solution for the case $h_1 = h_2 = h,\ E_1 = E_2$ is presented here:

$$\begin{pmatrix} \alpha \\ R \end{pmatrix} = \begin{pmatrix} \dfrac{6\Delta l}{13h} \\ \left(\dfrac{13}{12} \cdot l_0 - \dfrac{5}{24} \cdot \Delta l\right) \cdot \dfrac{h}{\Delta l} \end{pmatrix}. \tag{9}$$

Thus, we have an approximate equality for R at $h_1 = h_2 = h,\ E_1 = E_2,\ \Delta l/l <<1$:

$$R = \frac{13}{12} \cdot \frac{l_0 h}{\Delta l}. \tag{10}$$

To study the dependence of strain for the composite prepared by electrolytic deposition of nickel on temperature and cycle number (resource), the material was subjected to thermocycling. The sample was photographed both in martensitic and austenitic states after every hundred of cycles. The following results have been obtained by processing the images: R_{min} = 2.0 mm, R_{max} = 9.0 mm, N = 10; R_{min} = 2.3 mm, R_{max} = 8.5 mm, N = 200; R_{min} = 2.6 mm, R_{max} = 3.3 mm, N = 2000. Here, R_{min} is the composite curvature radius in the martensitic state; R_{max}, the same in the austenitic one; N, the cycle number. The curvature change ($R_{max} - R_{min}$) is defined by a considerable diminution of R_{max} and an insignificant increase of R_{min} as the cycle number increases. This can testify for accumulation of inelastic defects in the electrolytic nickel layer, while the $Ti_{50}Ni_{25}Cu_{25}$ SME ribbon is subjected to such accumulation to a considerably lesser extent.

The composite curvature in the austenitic state calculated using (10) at $\Delta l/L = 0.01$, h = 0.020 mm is R_{min} = 2.14 mm, while the corresponding experimental value is 2.6 mm. Thus, taking into account the assumptions adopted, the results are in a satisfactory agreement.

To conclude, a type of functional materials based on alloys with shape memory effect (ferromagnetic or non-ferromagnetic) is proposed designed as a layered structure consisting of an elastic layer and a SME one, the latter being pre-strained (stretched) pseudo-plastically. Such a composite material is characterized by a large reversible bending strain controlled by temperature (or by magnetic field if the SME layer is ferromagnetic) and is practically feasible and suitable for miniaturization. The samples of functional materials based on rapid-quenched $Ti_{50}Ni_{25}Cu_{25}$ alloy prepared by gluing and electrolytic deposition have been studied in experiment, and actuators controlled by heat field have been realized basing thereon. A model of actuator prepared by electrolytic nickel deposition demonstrated a strain about 1 % during 1000 cycles and more. A simplified mathematical model has been derived that relates the sample characteristics and its pre-strain value to the curvature radius in austenitic state and the forces generated. The experimental values of the actuator curvature agree satisfactorily with theoretical estimations using the mathematical model.

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Функціональний матеріал з пам'яттю форми, що демонструє гігантську оборотну деформацію

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Запропоновано та експериментально випробувано нову схему композитного функціонального матеріалу на основі матеріалу з ефектом пам'яті форми. Ця схема може бути застосована для більшості традиційних матеріалів з пам'яттю форми — феромагнітних та неферомагнітних сплавів, а також полімерів. У всіх випадках вона забезпечує гігантську оборотну деформацію, хоч використовується лише "односторонній" ефект пам'яті форми. Ця схема є особливо перспективною для застосування у галузі мікро- та наномеханіки.