# On the Energy Dissipation Capacity and the Shape Memory. A Comparative Study between Polymer Composites and Alloys

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Damping capacity is comparatively analyzed for a composite with polymer matrix (vinyl ester) and a shape memory alloy (copper-zinc-aluminium). A good damping capacity of shape memory alloy results in structural transformation domain in detriment of composite material. The theoretical model developed on the analyzed material behaviour describes qualitatively the temperature dependence of the dissipation capacity.

Keywords: polymer, shape memory alloy, dissipation capacity, fractal

Due to the increased need for the materials with high damping performance, an important progress has been achieved in the analysis of damping of composites, especially in polymer composites [1–4]. Damping is a measure of energy dissipation in engineering materials and structures, and it is an important parameter for noise and vibration control in advanced composite materials and structures. Some new models about the damping behaviour of polymer composites have been presented, among which the strain energy-based finite element techniques have been widely adopted, whereas the matrix and fibber are generally assumed to be linearly elastic in calculation [5–8]. On the other hand, as one of the most promising structure-function type damping materials, particulate- reinforced metal matrix composites (PMMCs) have attracted scientific interest [9–12]. In aerospace and many other lightweight structures, there are many vibration inputs that can lead to resonance [13], so it is necessary to have a sound methodology to control the vibration. In particular, the polymer composite, as a novel damping material, has attracted great interest in the development because of its excellent stiffness and damping characteristics [14]. In recent years, research on fly ash as a filler and reinforcement in metal-matrix composites (MMCs) and polymer-matrix composites (PMCs) has been growing [15-16].

Among the prevalent high damping metallic materials, shape memory alloys (SMAs) could be one of the most promising candidates due to their high damping capacity arising from the reversible martensitic phase transition (MT) and the stress induced reorientation of martensite variants [17,18]. It is generally accepted that micro structural defects should play a dominant role in the damping response of materials [19–22]. From this fundamental concept, a variety of high damping metals and alloys have been developed.

High damping capacity has been one of the most important properties of materials used in engineering structures where undesirable noise and vibration are to be passively attenuated. The resultant material can find use in a number of industrial areas, including lightweight structures and energy absorption apparatus, etc [23-24].

Shape memory alloys are in most of the applications represented by Ni-Ti alloys, especially for medical applications for their good corrosion resistance and biocompatibility and copper based alloys like Cu-Zn-Al, Cu-Mn-Al and Cu-Al-Ni. Because of their high dissipation capacity, Cu-Zn-Al alloys represent an interesting opportunity for vibration amortization or structure constructions. A phase named " $\beta$ " or "A" (austenite) under decreasing temperature influence is transforming in other phase named "M" (martensite). Transformation  $\beta \rightarrow M$  is considered directly martensitic transformation and  $M \rightarrow \beta$  is the inverse martensitic transformation.

Internal friction (tan d) for an experimental NiTi shape memory alloy fiber, measured during a heating cycle, is compared with the values for the resin, the matrix of the composite obtained and the composite in figure 1. The tan d for the shape memory alloy fiber in the austenitic state, is reduced by about 0.005, which is one-tenth of the value of 0.055 for the fiber in the martensitic state. This result is consistent with the reported values [25, 26]. Due to the use of log scale for Y-axis, normal scattering at low tan d values appears amplified [27]. The internal friction (tan d) for the vinyl ester resin is lower than that for the martensitic SMA and higher than that for the austenitic SMA. The tan d values for the SMA composites are between the limiting values for the resin and the fiber, except at the transformation temperatures and at temperatures above the  $T_g$  (113 °C) of the resin. It can be inferred from figure 1 that the temperatures required for reverse phase transformation from martensite to austenite of the SMA fibers in the composite and the SMA fibers superpose. A tentative interpretation of this result is provided below.

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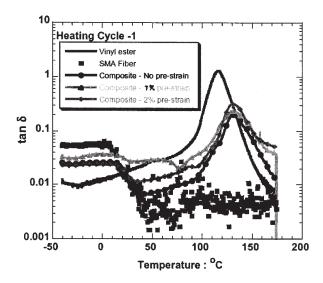


Fig. 1 Comparison of damping of a SMA fiber (NiTi), resin and composite during a heating cycle [27]

The microstructure of the purchased SMA fiber was a mixture of austenite and martensite that had not undergone complete reverse transformation to austenite due to the lack of adequate thermal energy at room temperature. The martensite formed from austenite due to forward thermal transformation is referred to as "thermal martensite" in this paper, to differentiate it from the martensite formed from austenite due to stress-induced transformation [27].

When the composite containing the SMA fibers with no pre-strain was cooled to 40°C for the DMA test (a first heating cycle), the austenite transformed to thermal martensite while the residual thermal martensite was unchanged. The damping capacity of the composite at this temperature is due to the damping capacities of the thermal martensite in the fiber and the vinyl ester. When this composite was heated, all of the thermal martensite underwent reverse transformation, yielding 100% austenite in the fibers at T > 35 °C. The damping capacity of the SMA composite with no pre-strain at T > 35 °C is due to damping capacities of the austenite and vinyl ester. Similar slopes for the curves in figure 1 for both the vinyl ester and composite suggest that the increased damping with temperature at T > 35 °C is due to the increased damping capacity of the vinyl ester. The peak in tan d at 113 °C is due to a peak in damping capacity of the vinyl ester resin. Since damping due to oriented martensite is higher than that due to austenite, the overall damping capacity of the composite is higher than that of the composite with no pre-strain.

In the present paper experimental and theoretical investigations on damping capacity between composite material with polymer matrix (vinyl ester) and a shape memory alloy type Cu-Zn-Al are performed.

### **Experimental part**

A shape memory alloy, with good memory properties, was analyzed by internal friction point of view. Chemical composition was determined through spectrometry analysis using Foundry Master equipment doubled by an EDAX, by Bruker, equipment for small areas and the microstructure with a scanning electron microscope (SEM) by Vega Tescan brand with a Secondary Electrons detector. Tensile testing of the alloy was accomplished using INSTRON's 8562 servo-electric testing machine.

To investigate the behaviour of a material during heating with respect to its physical dimensions, we use a dilatometer equipment type DIL 402. The measuring system employs two high resolution inductive displacement transducers; with its design using low-expansion invar and broad thermostatic control for highest accuracy, reproducibility and long term stability, it is capable of application temperatures up to 1600°C.

The versatility of the DMA 242 C is particularly obvious from the variety of sample holders. Depending on the type and consistency of your sample, you can investigate the visco - elastic properties accurately over a wide modulus range. The DMA 242 C operates in the broad temperature range of -170 to 600°C. The low-temperature range is achieved with the proven, low-consumption CC 200 L liquid nitrogen cooling system.

Frequencies from 0.01 to 100 Hz can be selected and combined with defined stress of up to 16 N and deformation amplitudes of between 0.1 and 240  $\mu m$ . The digital filtering via Fourier analysis yields an excellent signal-to-noise ratio, which means that even the smallest tan  $\delta$  values can be resolved.

By classical melting method a shape memory alloy based on Cu-Zn-Al was obtained. Besides the principal chemical elements, copper, zinc and aluminium, with our support other chemical elements like iron, lead or nickel appear in the composition, in reduced percentages for damping capacity improvement [28]. Because of chemical non-homogenization of material melting, the shape memory alloys before plastic deformation are prepared with some thermal treatments produced by diffusion in initial phase domain ( $\beta$  or  $\gamma$ ) [29].

Homogenization heat treatment applies to melted samples pursuit not only the homogenization of chemical composition but also the obtaining of soft martensitic structures imposed by cold form education necessity.

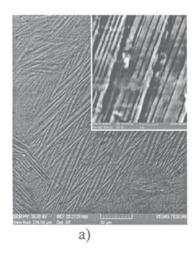
For these reasons after a heating at 800°C and a 6 h maintaining, a water cooling will limit the  $\gamma_2$  phase formation that is brittle and for a better plasticity. This thing is essential for form education. Necessary heat treatments were applied in an electrical oven LBS 6/04.

The material is in a deformed, by hot forge, form and heat treated by water quenched, realized through heating to 800°C, maintained 30 min and fast cooled in water. Chemical composition of material is presented in table 1,

 Table 1

 CHEMICAL ANALYZE OF DEFORMED SHAPE MEMORY ALLOY Cu-Zn-Al

Element	AN	Series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Oxygen	8	K-series	3170	7.997291	2.23962	20.01709	1.392909
Aluminum	13	K-series	6697	4.694356	5.349608	6.967403	0.279036
Cooper	29	K-series	135543	66.91326	69.57384	42.16825	1.691617
Zinc	30	K-series	29473	16.66711	15.08805	10.20729	0.793381
Lead	73	L-series	8999	6.539313	2.919772	1.447239	0.613761
Nickel	28	L-series	342	2.028704	1.836503	0.436299	1.00442
Iron	26	L-series	424	0.732828	3.543673	0.368373	1.00354
			Sum:	110.4656	100	100	



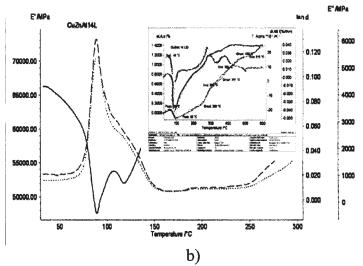


Fig. 2 Shape memory alloy Cu-Zn-Al characterization of forged state a) SEM microstructures for different magnifying powers 1000x and 5000x in detail b) internal friction (tan d) and Young's modulus parts variation with temperature, in detail is presented the material behavior with temperature

in atomic and weight percentages. The oxygen gain in composition is on account of processing stage especially when hot forge applied.

Recently a group of researchers investigated the damping properties of CuZnAl alloys and reported a high level of amortization on these materials [30]. Martensite formation takes place starting from mono-crystal  $\beta$  phase producing a number of martensitic domains having each different indexes of habitual plans but crystallographic equivalents domains that will appear distributed in the entire sample, 24] these martensitic domains are named variants.

Because internal friction depends on deformation degree, the sample was analyzed in deformed state, the material having the microstructure characterized by plate variants as shown in figure 1. In the copper based shape memory alloy microstructures presented in figure 2, can be observed the dimension of grains, grains boundaries and martensitic plates, which are around 250, 0.10 respectively  $1.75 \, \mu m$  after an average of 50 measurements.

Martensitic plates from Cu-Zn-Al shape memory alloy have a structure with internal defects made by invariant plane shearing; plate accommodation in austenite matrix is done by macla formation to keep the crystalline network coherence on martensite-austenite interface. For this reason, it can be appreciated that observed macla in this alloys structure are of accommodation nature and not transformation, further more it must be retained that almost 50 % are of type II just like on shape memory alloys based on Cu-Al-Ni [31].

Concerning the internal friction of the material, specific samples were thermally analyzed by dilatation properties and mechanical – dynamic behaviour with temperature variation.

In figure 2 b, in detail, there are represented the variations of dilatation relative thermal coefficient (dL/L $_0$ ) in % with continuous line, time derivate of relative thermal coefficient dL/dt in %/minutes, represented with blue discontinued line and dilatation thermal coefficient with red color, all with respect to the temperature. The test took place in helium atmosphere He50 from 305 to 913 K with a heating rate of 5 K/minute using a condense silica sensor, for a cylindrical shape of sample with 25.6 mm in diameter and 25 mm length.

Since at the beginning of heating a big contraction of the material is registered, contrarily to metallic materials behaviour around 100 °C, this can be appreciated that it appears by martensite reverse contribution. From internal friction point of view we are interested more on transformation temperatures range than transformation temperatures themselves, so we observe a range between 66 and 96 °C range where an internal friction peak supposes to appear according to [32-34].

After the thermal behaviour determination, the material was investigated concerning his mechanical-dynamic variation with temperature using a rectangle sample with 20x7.95x0.55 mm dimensions, on a three points bending support with a 5K/min temperature rate in a temperature range from 32.5 to 302 °C at 1 Hz frequency. The resulted diagram, presented in figure 2 b, reveals a strong connection between the transformation temperature range and the appearance of an internal friction peak.

Along with the internal friction variation, represented by tan d, with blue dashed line in the resulted diagram is also presented the real part E' of elasticity modulus with black continuously line and imaginary part, E'' with dashed red line. Internal friction peak appears at 90.88028 °C temperature having an increase value of 0.11635 in the same time, a 3 °C earlier, with an important decrease of the storage modulus from 66000 to a minimal 47556.07277 MPa value.

Another modification of internal friction variation and storage modulus is observed around 393 K but with reduced values, variations that can be considered the equipment noise or existence of some small cracks in the material that will influence the results diagram. In martensitic shape internal friction decreases around 0.02 but anyway bigger than austenitic phase were internal friction is around 0.015.

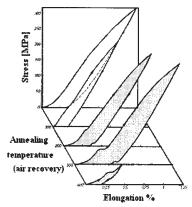


Fig. 3 Superelasticity appearing under plateau on discharge observed on traction curves of homogenized Cu-Zn-Al alloy along with annealing temperature increasing

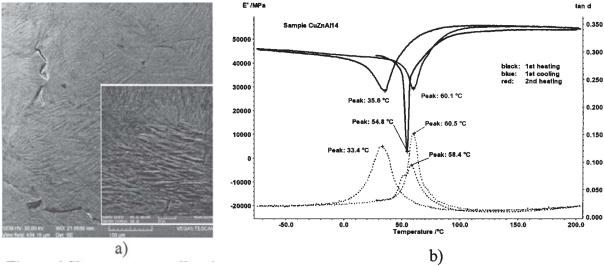


Fig. 4 Shape memory alloy Cu-Zn-Al characterization of tensioned state a) SEM of Cu-Zn-Al, 500x and 5000x in detail b) variation diagram of internal friction, tan d, and storage modulus, E' with temperature

On this alloy super-elasticity property appears with the increasing of annealing temperature applied after homogenization as it can be observed from figure 3 where there are represented the elongation curves %, as function of the applied stress in MPa but also as function of the annealing heat treatment applied.

Material study from internal friction point of view continues with analysis of 4 % traction deformed samples from hot laminated form.

In figure 4 there is presented the electronical microscopy of traction deformed samples, analysis realized immediately after the traction test without electromechanical preparation. The martensite has a smooth structure with dislocations and a small proportion of packaging defects or macla's.

After studies with electrons diffraction on a selected area and electronic microscopy the tension induced crystals martensite structure was identified as type 18R (18  $R_1$ ) the same as  $\beta_1$ ' martensite induce thermal in binary alloy Cu-Al.

# Results and discussion

Different martensitic plates orientate themselves, most of the times in function of the applied tension orientation. For these reasons more the deformation sum increases, more the dislocations number increase in order to improve the accommodation and the deformation propagation. The appearance and reach of dislocations help the dissipation capacity of mechanical energy applied in thermal energy.

Traction deformed samples by Cu-Zn-Al shape memory alloys were analyzed concerning the dynamic mechanical behaviour through DMA tests. Tests took place on rectangular samples 30x10x0.5 mm by heating from -50 to  $200\,^{\circ}$ C in two heating cycles and one cooling cycle. The variation of the internal friction, tan d, represented with dotted line and real part of Young modulus, E with full line with temperature, presented in figure 6, reveal some modifications in alloy behaviour due to internal transformation phases. Using a dilatometer test for transformation temperatures determination, an internal friction peak was expected around  $50\,^{\circ}$ C to appear on DMA diagram.

Corresponding to martensitic transformation an internal friction peak appears at 331.4 K having a good value around 0.15 accompanied by a decrease in the elasticity modulus with an extremely reduced peak around 2000 MPa at 327.8 K.

On cooling the material improves his internal friction value to 0.13 with a peak appearance temperature modification, to the left side of the diagram, in the same time to 306.4 K. The storage modulus decreases around the 307.5 K temperature, but not as strong as for heating, conducts (only) to a 28000 MPa value.

At the first heating cycle the internal friction peak seems to be formed by two reduced peaks, one around 50 °C with a value of 0.085 and the big one around 54.8 °C showing a higher peak in temperature domain. The second cycle reveals a single peak of internal friction that stabilizes at 60.5 °C with a bigger value of 0.151 but on a reduced area comparing to first heating peak.

The storage modulus decreases again, near the internal friction peak temperature, specific at 60.1 °C, but not that obviously as in first case, from 50000 MPa values to 30000 MPa values.

According to these results a new material, a copper based shape memory alloy, can be considered as solution for reinforcement elements in polymer matrix composite.

## Theoretical model

We can admit that the total loss angle for shape memory alloy,  $\delta_{\scriptscriptstyle G}$ , consist as a sum of two angles, one corresponding to martensite structure,  $\delta_{\scriptscriptstyle M}$ , and the other corresponding to austenite structure,  $\delta_{\scriptscriptstyle A}$ . Then we shall have :

$$tg\,\delta_G = \frac{tg\,\delta_M + tg\,\delta_A}{\left|1 - tg\,\delta_M tg\,\delta_A\right|} \tag{1}$$

together with expressions

$$tg \, \delta_G = \left(\frac{\eta}{E}\right)_G \omega; tg \, \delta_M = \left(\frac{\eta}{E}\right)_M \omega; tg \, \delta_A = \left(\frac{\eta}{E}\right)_A \omega, \quad \text{(2a-c)}$$

where  $\omega$  represents the movement pulsation and G, M and A the material states, general, martensite or austenite [25]. By placing relationships (2a-c) in expression (1) is obtained the equation

$$tg \,\delta_G = \frac{\left[ \left( \frac{\eta}{E} \right)_M + \left( \frac{\eta}{E} \right)_A \right] \omega}{\left[ 1 - \left( \frac{\eta}{E} \right)_M \left( \frac{\eta}{E} \right)_A \omega^2 \right]} \tag{3}$$

with  $\eta$  the imagin<u>ary</u> part and E the real part of complex elasticity modulus  $E = E + i\eta$ .

Since the structure of the mixture of martensite - austenite is equated with a "fractal" fluid, occurs the dependence  $\omega = kT/mD$ , [35-36], where m is the "mass" of fluid particle, D is the transfer coefficient of fractal - nonfractal evolution, T is absolute temperature and k is Boltzman constant.

Taking into account the notations

$$\sqrt{\left(\frac{\eta}{E}\right)_{M}\left(\frac{\eta}{E}\right)_{A}} \frac{k}{mD} = \frac{1}{T_{0}}; \frac{\left[\left(\frac{\eta}{E}\right)_{M} + \left(\frac{\eta}{E}\right)_{A}\right]}{\sqrt{\left(\frac{\eta}{E}\right)_{M}\left(\frac{\eta}{E}\right)_{A}}} = \gamma = const.; t = \frac{T}{T_{0}}$$
(4 a-c)

and after a simple calculation, the expression (3) becomes

$$tg \, \delta_G = \frac{\gamma \cdot t}{\left|1 - t^2\right|} \tag{5}$$

Equation (5) represents a normalized temperature dependence of damping capacity and her graph is

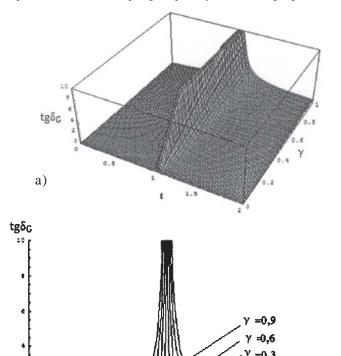


Fig. 5. Function dependence of damping capacity with temperature representation a) 3D and b) 2D

presented in figure 5 a, b paying respect for material properties.

Generally can be done different dependence between  $\omega = \omega(t)$ , using this fact we obtain a big variety of mathematical models [37-38]. In this paper is considered the simplest case of a linear dependence. Comparing with experimental results, figure 2 or 4, the mathematical model, represents a good approximation of the physical behaviour. Knowing the material characteristics,  $\gamma$ , the variation behaves differently as internal friction dependence of temperature but well described by function (5).

Finally, we remember that we will study, in a future work, the complex behaviour of these materials in the manner specified and developed in some previous papers [39-42].

#### **Conclusions**

Idea of this study was based on intuition of a composite material property with polymeric matrix and reinforced shape memory elements for very good damping properties and usage in many applications like automotive or aerospace industry.

A shape memory alloy based on copper was analyzed by his internal friction point of view with nice value of damping capacity in martensitic temperature transformation range.

The material internal friction increases with the tension degree and the transformation domain moves to the left side of temperature axis.

Comparing to a composite material behaviour the shape memory alloy exhibits a bigger peak of internal friction in martensitic transformation range which can be improved by a polymer matrix of the material.

The theoretical model obtained presents a nice approximation of shape memory alloys behaviour with temperature regarding the variation of its internal friction.

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