Internal Friction Phenomena at Polymeric and Metallic Shape Memory Materials. Experimental and Theoretical Results

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The internal friction phenomenon in metallic and polymeric shape memory materials is analyzed. The experimental results permit validation of a theoretical model which describes qualitatively the temperature dependence of the internal friction for the investigated materials. Moreover, theoretical model accepts not only evaluations of different states of material (solid state structural transformations as martensite – austenite) but also materials very different as nature (metallic or plastic).

Keywords: shape memory polymers, damping capacity, internal friction, martensitic transformation

In this paper, we present and compare materials such as crystalline solids and amorphous solids, which are strongly different in the classical conception. Although they are categorically rigid materials, in terms of microstructure they show fundamental differences. Thus we feel the need to explain the terminology used.

The crystalline solid is a rigid material having the regular internal arrangement of atoms, ions, or molecules characteristic to crystals. Crystalline materials do not need to necessarily exist as crystals, but dispose of an uniform atomic structure throughout the entire material. For example, all metals are crystalline although they are not usually seen as regular geometric crystals. For this reason the most intuitive definition says that the constituent parts of this solid type have a simple and definite geometric arrangement that is repeated in all directions.

The amorphous solid is a rigid material whose structure lacks crystalline periodicity; that is, the pattern of its constituent atoms or molecules does not repeat periodically in three dimensions. In the text of the article, the amorphous and noncrystalline words are synonymous. The most familiar amorphous solids are, for example, the oxide glasses (generally, the silicates) and the glassy polymers (plastics). However, as a state of matter, amorphous solids are much more widespread than just the oxide glasses. There are organic (polyethylene and some hard candies) and inorganic (the silicates) amorphous solids.

Shape memory materials are defined by their capacity to exchange their shape with temperature variation by storing a deformed (temporary – hot form) shape and recover an original (parent – cold form) shape. The shape memory behaviour is typically induced by a change in temperature and has been observed in metals, ceramics, and polymers [1-3]. Owing to their unique shape memory mechanism, the shape memory effect in polymers differs from that observed in ceramics and metals. Shape memory polymers (SMPs) experience lower stresses during deformation and demonstrate much larger recoverable strains. A shape memory polymer can be a thermo-set or thermoplastic with a chemically or physically cross-linked network structure, which permits a rubbery plateau at a temperature above the glass transition temperature, $T_g$. One benefit of SMPs is that $T_g$ can be easily tailored by the control of chemistry and structure [4-7].

The design of SMP-based devices demands thorough characterization and constitutive modeling of the thermo-mechanical shape memory cycle. Constitutive models facilitate the prediction of recoverable stress and strain levels under varying degrees of constraint, as will be invariably experienced in SMP applications. In addition, advanced SMP applications require optimized storage and recovery properties achieved through a fundamental knowledge of the constitutive relationship for various thermo-mechanical conditions.

Early applications of the shape memory effect in polymers included heat shrinkable tubes, wraps, foams and self-adjustable utensils. Recently, substantial research efforts on SMPs are emerging in the areas of biomedical devices, deployable space structures, and microsystems [8,9].

The mechanical properties of polymeric materials are strongly temperature dependent [10-11]. An amorphous polymer that is stiff at room temperature can become quite compliant and behave in a ductile, rubbery manner at higher temperatures. The transition from high stiffness to low stiffness occurs at the glass transition temperature, $T_g$. In figure 1, the storage modulus, loss modulus and tan delta of an epoxy resin are plotted versus absolute temperature.

The general behaviour observed in figure 1 is characteristic of amorphous thermoset polymers with appropriate cross-linking density. All such polymers show
a similar response as a function of temperature, referenced to their respective \( T \). The properties of such polymers near \( T_g \) account for the shape memory behaviour during a thermo-mechanical cycle. At temperatures well above \( T_g \), the polymer is in the rubbery state. The stiffness of the polymer is low, and the deformation energy is converted into a free conformational entropy change. With appropriate cross-linking density, rubbery elastic strains can be on the order of several hundred percent.

In the rubbery state, the elastic deformation of an ideal network polymer produces a change in the conformational entropic state of the polymer chains, and the interaction between chain molecules is relatively negligible. When \( T < T_g \), the large-scale conformational changes are not possible but localized conformational motions are allowed. At temperatures well below \( T_g \), the polymer is in the glassy state and behaves as an elastic solid at small strains. The low temperature elasticity is due to primary bond stretching, which causes a change in internal energy. In both the glassy and rubbery states, the elastic strain can be stored "instantaneously" and released "instantaneously" upon removal of the applied stress. The damping factor (Tan delta) in these two states is relatively small compared to that in the glass transition region (figure 1), in which viscoelasticity governs the deformation and recovery in the time scale considered.

A shape memory alloy (SMA) is a metallic material which, in relation to the diffusion less martensitic phase transformation, may exhibit the shape memory effect or the superelastic effect (SE). The SE is associated with a large nonlinear recoverable strain upon loading and unloading, where an increasing stress applied to austenite gradually induces a considerable strain and the associated transformation into martensite. When the force is removed, the reverse martensitic transformation takes place, and the original material shape is recovered. Moreover, in both effects, energy dissipation (damping) is observed during load-unloading cycles. In the stress-free state, a SMA is characterized by four transformation temperatures: \( M_f \) and \( M_d \) during cooling, and \( A_f \) and \( A_d \) during heating, \( M_f \) and \( M_d \) indicate the temperatures at which the transformation to martensite starts and finishes, respectively, \( A_f \) and \( A_d \) indicate the temperatures at which the inverse transformation starts and finishes, respectively. Moreover, above a temperature, usually called \( M_f \), the stress induced martensitic transformation will not occur, because of the stability attained by austenite.

Thus, for the SE to occur, stress should be applied within a temperature range between \( A_f \) and \( M_f \) with \( A_f < M_f \). The damping behaviour exhibited by superelastic materials makes them promising candidates to be used in seismic-energy dissipative devices. Although several shape memory alloys have been characterized, only few studies, using Cu-based SMA alloys, have been performed that are expected to lead to seismic applications [12]. In this case, it is desirable that the superelastic behaviour occurs at ambient temperature. In addition, the material should dissipate substantial seismic energy through repeated stable cycles at large strains with small degradation in properties and low sensitivity to frequency in the 0.1–5 Hz range. Moreover, to avoid intergranular brittle fracture, a small grain size is needed. Although the main factor controlling the temperature at which phase transformation takes place is alloy composition, other factors such as heat-treatment, quenching rate and grain size also affect this critical temperature [13].

In the present paper experimental and theoretical results of internal friction phenomena in polymeric and metallic shape memory materials are obtained. It is shown that theoretical model permits a ‘dynamics’ of internal friction phenomena function of temperature for a big materials diversity like polymers, metallic materials and especially shape memory alloys.

**Experimental part**

Investigated shape memory alloy, copper-zinc-aluminum, obtained by classical melting method, have the chemical composition presented in table 1, with respect to oxygen, nitrogen or carbon from the exterior layer formed in contact with air.

Tested materials were studied structurally with an optical metallographic microscope, Vega Tescan LMH II type with a secondary electrons detector, to make a point about martensitic variants characteristic of shape memory alloys from the structures.

<table>
<thead>
<tr>
<th>Element</th>
<th>AN</th>
<th>series</th>
<th>Net</th>
<th>[wt.%]</th>
<th>[norm. wt.%]</th>
<th>[norm. at.%]</th>
<th>Error in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>6</td>
<td>K-series</td>
<td>1605</td>
<td>3.310917</td>
<td>0.308415</td>
<td>14.12143</td>
<td>0.68667</td>
</tr>
<tr>
<td>Oxygen</td>
<td>8</td>
<td>K-series</td>
<td>602</td>
<td>1.624274</td>
<td>0.62046</td>
<td>5.20074</td>
<td>0.45232</td>
</tr>
<tr>
<td>Aluminum</td>
<td>13</td>
<td>K-series</td>
<td>6295</td>
<td>5.340992</td>
<td>6.36956</td>
<td>10.14063</td>
<td>0.311646</td>
</tr>
<tr>
<td>Copper</td>
<td>29</td>
<td>K-series</td>
<td>148903</td>
<td>68.9052</td>
<td>73.85314</td>
<td>55.54865</td>
<td>1.734839</td>
</tr>
<tr>
<td>Zink</td>
<td>30</td>
<td>K-series</td>
<td>34203</td>
<td>18.13487</td>
<td>18.12117</td>
<td>14.20734</td>
<td>0.480848</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>73</td>
<td>L-series</td>
<td>4061</td>
<td>2.759362</td>
<td>0.757276</td>
<td>0.781204</td>
<td>0.367411</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td></td>
<td></td>
<td>100.0756</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>
The only method to evidence shape memory effect of a metallic material is dilatometry. The increase of solid dimensions phenomena at heating is named thermal dilatation, in this purpose some tests were realized on investigated alloys using a laboratory differential dilatometer type Netzsch Dil 402.

To study the internal friction, which is related to damping capacity of materials, a dynamic mechanical analyzer (DMA) type DMA 242 by Netzsch was used which registers besides the internal friction also storage elastic modulus values and loss elastic modulus (loss part by energy transformation) as well.

The material is analyzed in forged form, realized by hot deformation at 800°C, and heat treated by solution hardening, heating at 800°C, maintained 30 min and cooled in water [14].

Electronically microscopies of shape memory alloy, with electro-mechanically prepared surface and FeCl₃ attack, present martensitic variants, orientated in different direction, and with different shapes, like diamond, arrow or plates, presented in figure 2 a. Medium dimensions of grains are 200 μm and around 10 μm for martensite plates, after an average of 50 measurements with Tescan software.

Chemical composition represents a classical shape memory alloy based on copper-zinc with a small amount of aluminum for temperature transformation point's control. Thermal behavior of the material is made through dilatometry tests, heating the material at 350 °C with a 5 °C/min rate. At the beginning a strong contraction of the material occurs, presented in the dilatometry result in figure 2 b. This strange behavior for a metallic material is characteristic to shape memory alloys, the reverse martensitic transformation taking place in this temperature range. Temperature transformation points Aₜ and Aₑ appear at 132°C and 166°C and conforming to [15] in this domain an internal friction peak will be exhibited, function of martensite-austenite transformation rate. The registered contraction of this material in forged state is 0.01 % on a large temperature domain 34°C.

By damping capacity point of view the alloy was tested with a dynamic mechanical analyzer on a -50 to 200°C range temperature, with a 5°C /min heating rate and 1Hz frequency.

In figure 3, internal friction ($\tan \delta$) and storage modulus ($E'$) variations with temperature are presented after two heating and a cooling cycle. For the first heating cycle represented with black color, dashed for internal friction and filled line for storage modulus, an IF peak appears at 150°C made by two actually parts with reduced values near to 0.07 on a 20°C temperature range. Martensitic IF has reduced values around 0.02 for the first cycle and an increase on cooling branch and for the second heating almost to the first peak obtained, at a value of 0.07 which is higher than internal friction for austenitic range characterized by a 0.04 value. Weak properties of this shape memory alloy reveal no other IF peak suffering a stabilization. The storage modulus behave a decrease connected to first appearance of the IF peak to 70000 MPa value and for second heating cycle a stabilization with a small variation around 120 °C.

Because of the poor results registered in deformed state we can appreciate that a tensioned state of the material, at least 4% will raise the damping capacity towards practical application values [16].

Results and discussion
Experimental results
The results after loading-unloading cycles in different states of shape memory alloy CuZnAl, water quenched and recovered, hot laminated or forged are presented in figure 4 and it can be seen that material exhibits a superelastic behavior characterized by the presence of tension plateaus, at loading but also with discharging phenomena met in reversible martensitic transformation induced by tension [17]. With the number of loading-unloading cycles increase the resulted curves tend to approach transforming themselves in loops, figure 4 c or d.
It is clear that the forged sample is more ductile than the laminated one, figure 4 a. Also with increasing of the recovery temperature from 100 °C to 200 °C, the mechanic hysteresis considerably enhances and proportional increased with the surface between loading and unloading of tension curve. In figure 4 (c) and (d) it can be considered that water cooling increases internal friction comparing with air cooling. Figure 4 d shows that after mechanic cycling until 150 MPa, the hysteresis loop closes after 5 cycles.

Dilatation of material in tensioned state, presented in figure 5 a, confirm the memory effect exhibit in temperature transformation points, between 78 °C and 115 °C with a bigger effect, and in other temperature ranges, structure modifications in solid state phenomena’s catch on internal friction and storage modulus variation with temperature also, figure 5 b).

The internal friction variation with temperature, represented in figure 5 b, shows values of 0.03 for martensitic state of material until around 78 °C, a smaller value, 0.02 for austenitic range and exhibits a dissipation peak definitely in martensitic – austenitic domain put on transformation behaviour.

Internal friction reach a peak at 103°C with a value of 0.09 far from practical application values, but which can be really improved using this material as reinforcement fibers and a polymer like epoxy resin presented in introduction, as matrix. Loss modulus decreases in transformation range reaching a 65000 MPa from an 85000 MPa value at 102°C, always with few °C degrees before the internal peak appearance [16].

Characterized from martensitic transformation point of view, the internal friction peak obtained around 100 °C is influenced by martensite-austenite transformation rate. Even if the peak maximum value is reduced, this alloy has the advantage of an extended temperature domain, 37 ° where the material exhibits good damping properties.

Comparing with the same material in deformed state in tensioned 4% case, an improve of dissipation capacity can be observed in the same time with the movement of the martensitic temperature transformation points with 60 °C to the left, including the appearance of internal friction peak. This behaviour of shape memory alloys, paying respect to the internal friction property, with different values for those 3 different states of material with temperature, martensitic, austenitic or transition martensite to austenite structural shapes is observed on shape memory polymers as well, in this case taking into account the domains made by glass transition temperature, characteristic to these materials.

Given the complexity of materials behaviour and the fact that we have information at the microscopic level (SEM microscopy, etc.) which can be easily used for advanced analysis [18], we intend to continue this study in terms of...
special mechanical tests [19,20], which increase the depth of investigation.

**Theoretical interpretation of results**

In practical cases internal friction determination is realized with oscillatory processes (torsion pendulum, no auxiliary mass oscillatory system, sound absorption). For this reason physical characteristics that define internal friction are from oscillation domain. We will consider next small amortizations and an independent internal friction of oscillation amplitude.

Because in oscillation amortized mode [21], a phase angle (of force before deformation) appears between force and deformation [22] in follow-up we will extend these results to a deformable continuously medium. Having specific tension (σ) and deformation (ε) variation in time in a certain point of a deformable continuously medium we got the specific oscillations with quasi-harmonic pulsations given by equation (1 a,b).

\[ \varepsilon = \varepsilon_0 \cdot \cos \omega t, \quad \sigma = \sigma_0 \cdot \sin \omega t \quad (1a,b) \]

where phase angle between tension and specific deformation

\[ Q^{-1} = \frac{\delta}{\omega_0} = \frac{2\beta}{\omega_0} \quad (2) \]

or even

\[ Q^{-1} = \sin \delta = \delta \frac{2\beta}{\omega_0} \quad (3) \]

is an internal friction consequence and consists a measure of here. 

Q\(^{-1}\) notation was adopted for internal friction as analogy with inverted quality factor of an electrical circuit.

Being calculated the logarithmic decrement of oscillation using the angle phase we obtain

\[ \theta = \ln \left( \frac{e^{-\beta}}{e^{-\beta \omega}} \right) = \beta T = \frac{\omega_0 \cdot \delta}{2} \quad (4) \]

from that result \(Q^{-1} = \omega_0/\pi\) so as a measure of internal friction can be used the logarithmic decrement paying respect for circle constant (distributed at π).

Because internal friction finds here origins in energy dissipation, a dependence it is expected to exist between dissipated energy and \(Q^{-1}\). To establish this relation we observe that oscillation energy can be expressed, at a certain moment, as maximum potential energy. Considering the amplitude \(A\) we have:

\[ W = \frac{k \cdot A^2 \cdot e^{-2\beta t}}{2} \quad (5) \]

Dissipated energy on a cycle is (in absolute value) equal with:

\[ \Delta W = \frac{1}{2} \cdot A^2 \cdot e^{-2\beta t} - \frac{1}{2} \cdot A^2 \cdot e^{-2\beta(T+\tau)} = W(1 - e^{-2\beta t}), \quad T = \frac{2 \cdot \pi}{\omega_0} \quad (6a,b) \]

Expanding in series the exponential function and paying respect to the small value of \(\beta\) we find that

\[ \Delta W = W(1 - 2\beta t + ... ) = 2\beta TW = 20W \quad (7) \]

so we can appreciate that

\[ Q^{-1} = \frac{1}{2\pi} \frac{\Delta W}{W} \quad (8) \]

Internal friction is, therefore proportional with dissipated energy in a cycle reported to all oscillation energy. Internal friction can be determined for forced oscillations; equation of these in material point model is

\[ \ddot{x} + 2\beta \dot{x} + \omega_0^2 x = \gamma \cos \Omega t \quad (9) \]

\(\gamma\) being the perturbation force amplitude reported to mass unit and \(\Omega\) the pulsation. In stationary regime the oscillation amplitude is

\[ A = \frac{\gamma}{\sqrt{(\omega_0^2 - \Omega^2)^2 + 4 \beta^2 \Omega^2}} \quad (10) \]

and it passes through a maximum point at resonance that occurs for a small \(\beta\) at \(\Omega = \omega_0\).

Assimilating now the network phononic with thermal fractal excitations (for details can be consulted references [23,24]) by notations

\[ \omega_n = \frac{k T_n}{m D}, \quad \Omega = \frac{k T}{m D} \quad (11a,b) \]

were \(k\) is Boltzmann constant, \(m\) represents the “entity” mass of fractal fluid, \(D\) the transfer coefficient of fractal – non-fractal, \(T_n, T\) are associated temperatures of phononic excitations \(\omega_n\) respectively \(\omega\), with notations

\[ \delta = \frac{2\beta m D}{k T}, \quad Q^{-1}_n = \frac{2\beta T}{A \omega_n}, \quad Q^{-1} = \frac{1}{\sqrt{(1 - \delta^2)^2 + \delta^2 \cdot \gamma^2}}, \quad F(t) = \frac{Q^{-1}}{Q^{-1}_e} \quad (12a-d) \]

Equation (10) takes the next form

\[ F(t) = \frac{1}{\sqrt{(1 - \delta^2)^2 + \delta^2 \cdot \gamma^2}}, \quad \Omega = \omega_0 \]

Dependences \(F=F(t,\delta)\) respectively \(F=F(t,\delta=\text{constant})\) are presented in figure 6.

Having the material characteristics known, through \(\delta\) coefficient, we can appreciate the damping behaviour for different material temperatures points characterizing all shape memory material states like martensite, austenite or martensite-austenite transition for alloys or before and after glass transition at polymers, taking in account the martensitic temperature transformations points, respectively the glass transition temperature.
Conclusions

Shape memory materials exhibit an internal friction peak in structural transformation domain with good values for applications as dissipation elements. By deforming the shape memory alloy, the transformation point moves to the left of the temperature scale taking the damping peak on the same area which also suffers an increase. Shape memory polymers also present an internal friction peak in glass transition temperature area.

Reanalyzing the polymer behaviour with a high internal friction ($\tan \delta$) peak at 60°C, almost 0.8, we can consider proper to obtain a composite material with matrix polymer (discussed resin) and a shape memory alloy as reinforcement elements, which will raise a material with high damping properties on a large domain of temperature, 40-120°C.

The theoretical model represents constantly both shape memory materials behaviours with temperature, being influenced by material properties, $\delta$. The mathematical model characterizes different material states, function of temperature and many materials from shape memory class like alloys or polymers.

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