Mechanical Spectroscopy of Nanostructured Composite Materials.

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Abstract. The thermo-mechanical behavior of different nano-structured composite materials, which were processed within the SAPHIR European Integrated Project, has been characterized by mechanical spectroscopy. The obtained results show clearly that creep resistance of fine grain ceramics such as zirconia can be improved by carbon nano-tube (CNT) reinforcements. On the other hand the elastic modulus and the damping capacity of aluminum matrix composites were increased by SiC nano-particle additions. It has also been observed that CNT additions are responsible for a better thermal stability of polymer such as ABS (Acrylonitrile-Butadiene-Styrene) used in automotive industry.

1. Introduction
Industrial equipments, particularly advanced technologies, operate more and more in extreme conditions and must be resistant to extreme temperatures, high pressure, shocks or mechanical vibrations. Examples of applications requiring highly resistant materials are turbines, engines, heat exchangers, automotive and aerospace components.

Research is based on the statement that all the existing materials are far from being tailored to the new stringent environments and consequently is focused on developing new better adapted materials. The materials, which have been investigated in the SAPHIR project, are nano-structured composites with different type of matrices: ceramic, metal or polymer. This kind of materials can bring a solution for optimizing different properties in the same material such as toughness and creep resistance, high temperature stability and high thermal conductivity, high hardness and high wear resistance. New nano-structured materials have been processed, which exhibit improved physical and mechanical properties at room temperature. However it was very important to characterize their thermo-mechanical behavior.

Mechanical spectroscopy [1, 2], which consists in measuring the complex elastic modulus, is a non-destructive technique well suited to the study of the temperature behavior of solids. For instance, the technique has produced very interesting results concerning the mechanisms that control high temperature plasticity of ceramics [3]. Moreover it measures the damping capacity, which may play an important role in the toughness of hard materials [4]. A high damping capacity is good for decreasing the noise emitted by an engine, but also for improving the fatigue resistance of the vibrating components. It has been observed that new nano-structured ceramic matrix composites exhibit a high temperature mechanical loss spectrum composed of a low exponential background as an indicator of a good creep resistance, and possibly a superimposed damping peak accounting for toughness...
improvement or noise reduction. In metal matrix composites, the relaxation of the interface thermal stresses may be studied by the transient components of the mechanical loss spectrum [5] and the interface damage accumulation by the evolutions of the elastic modulus.

2. Mechanical spectroscopy.

2.1. Anelasticity

Mechanical spectroscopy is primarily associated with the anelastic behavior of solids. Anelasticity [1,2] is evidenced in the following simple experiment (Figure 1a). A stress \( \sigma \), of low intensity, is applied abruptly to a specimen at time, \( t = 0 \), and held constant while the strain, \( \varepsilon \), is recorded as a function of time. The instantaneous elastic strain is given by: \( \varepsilon_e = J_u \sigma \), where \( J_u \) is the unrelaxed compliance. The anelastic strain \( \varepsilon_a \) increases with time from zero to an equilibrium value \( \varepsilon_a^\infty \). When equilibrium is reached, \( \varepsilon = \varepsilon_e + \varepsilon_a^\infty = J_r \sigma \), where \( J_r \) is the relaxed compliance. This evolution from one equilibrium state to a new one, under an applied stress, is called anelastic relaxation, and may be defined by two parameters, the relaxation time \( \tau \), and the relaxation strength \( \Delta \):

\[
\Delta = \frac{\varepsilon_a^\infty}{\varepsilon_e} = \frac{J_r - J_u}{J_u}
\]

If, the stress is removed after a certain delay, one can observe the instantaneous recovery of the elastic strain and with the relaxation time \( \tau \), the recovery of the anelastic strain. In such an experiment, strain is completely recoverable.

From a microscopic point-of-view, the anelastic strain can be interpreted as being due to the movements of structural defects (elastic dipoles, dislocations, interfaces) from one equilibrium position defined at \( \sigma = 0 \) to another one defined at \( \sigma \). The relaxation strength, \( \Delta \), is then proportional to the concentration of defects, which are relaxing, the relaxation time \( \tau \) accounting for their mobility.

![Figure 1.](image)

**Figure 1.** a) Elastic \( \varepsilon_e \) and anelastic \( \varepsilon_a \) strain of a solid submitted to stress \( \sigma \).

b) Rheological model corresponding to the anelastic behavior of Figure 1a.

From a rheological point-of-view, the solid can be represented by the model shown in Figure 1b. The spring \( "J_r - J_u" \) in parallel with the dashpot of viscosity \( \eta \) is essential to the recoverable nature of the anelastic strain. If this spring does not operate, the anelastic strain does not reach an equilibrium value and is then no longer completely recoverable: onset of plasticity.
The anelastic behavior in figure 1 is representative of the standard anelastic solid [1,2], the equation of which is:
\[ \varepsilon + \tau \cdot \dot{\varepsilon} = J_r \cdot \sigma + \tau \cdot J_u \cdot \dot{\sigma} \] (2)

Measurements performed in the way described in figure 1 are very delicate, and it is more convenient to use in practice dynamic methods for measuring the relaxation parameters. If an alternative stress, of circular frequency \( \omega \), \( \sigma = \sigma_0 \exp(i\omega t) \) is applied to the system, the linearity of the stress-strain relationships assures us that strain \( \varepsilon \) is periodic with the same frequency:
\[ \varepsilon = \varepsilon_0 \exp[i(\omega t - \delta)] \] where \( \delta \) is the phase lag of strain behind stress (due to anelasticity). Introducing these expressions of \( \sigma \) and \( \varepsilon \) in equation (2) leads to the following relationship:
\[ \left[ \frac{J_1 \cdot J_r - J_2 \cdot J_u}{1 + \omega^2 \tau^2} \right] \cdot \sigma = \left[ J_1(\omega) - iJ_2(\omega) \right] \cdot \sigma = J^*(\omega) \cdot \sigma \] (3)

where \( J_1 \) and \( J_2 \) are, respectively, the real and the imaginary part of the complex compliance \( J^* \).

In metals and ceramics \( J_r \cdot J_u \ll J_u \), and the mechanical loss angle \( \delta \) is given by:
\[ \tan \delta = \frac{J_2}{J_1} = \Delta \cdot \frac{\omega \tau}{1 + \omega^2 \tau^2} \] (4)
and the variation of the dynamical compliance \( \frac{\Delta J}{J} \) due to anelasticity by:
\[ \frac{\Delta J}{J} = \frac{J_1(\omega) - J_2}{J_u} = \Delta \cdot \frac{1}{1 + \omega^2 \tau^2} \] (5)

The mechanical loss, \( \tan \delta \), presents a maximum as a function of \( \omega \tau \), centered at \( \omega \tau = 1 \). This maximum or peak provides the relaxation strength, \( \Delta \), (height of the peak) and the relaxation time, \( \tau \), (position of the peak on the \( \omega \tau \) axis). If several relaxation mechanisms are activated, the material exhibits a mechanical loss spectrum composed of damping peaks, which inform about microstructure dynamics. As most of the relaxation mechanisms are thermally activated,
\[ \tau = \tau_0 \cdot \exp\left(\frac{H}{kT}\right) \] (6)

\( H \) is the activation enthalpy. As a consequence, \( \tan \delta \) can also be measured as a function of temperature by holding \( \omega \) constant and the curve \( \tan \delta = \tan \delta(\text{T}) \) is the mechanical loss spectrum described as a function of temperature.

2.2. Mechanical loss spectrometer: the torsion pendulum

The most commonly used spectrometer for measuring the mechanical loss at low frequency is the inverted torsion pendulum (Figure 2). The torsion excitation is applied to the pendulum axis by means of Helmholtz coils acting on a permanent magnet fixed on the upper rod. Strain of the sample is measured by the deflection of a laser beam reflected on a linear photo detector by a mirror fixed above the sample. The photo detector is placed on a translation stage, which enables the correction of the static drift of the laser spot due to plastic deformation of the specimen. The sample is placed in a non-inductive tubular resistance furnace cooled by refractory screening and water circulation. The whole apparatus (except the lasers and photo detectors) is maintained under secondary vacuum (10^{-3} Pa). In order to avoid external mechanical vibrations, the pendulum is mounted on a damping frame. In a forced pendulum, the mechanical loss, \( \tan (\delta) \), and the shear modulus, \( G \), are measured from the phase lag and the amplitude ratio between the stress and strain signals, respectively. In a free pendulum, the
mechanical loss is deduced from the logarithmic decrement of the free decay of the oscillations and the shear modulus from the resonant frequency of the pendulum.

![Schematic drawing and picture of an inverted forced torsion pendulum.](image)

**Figure 2.** Schematic drawing a) and picture b) of an inverted forced torsion pendulum.

![Mechanical loss and elastic shear modulus as functions of temperature in 2Y-TZP zirconia.](image)

**Figure 3.** Mechanical loss (tanδ) and elastic shear modulus (G) as functions of temperature in 2Y-TZP zirconia as they can be measured in an inverted torsion pendulum.

As an example, Figure 3 shows a typical mechanical loss spectrum (tanδ and elastic shear modulus G=1/J) measured as a function of temperature in fine-grained zirconia (2Y-TZP: fully tetragonal zirconia stabilized by 2 mol % of yttria) [9,10]. The mechanical loss spectrum of TZP zirconia is composed of a damping peak at about 350 K associated with a modulus defect, and of an exponential increase in damping associated with a steep decrease in the shear modulus at high temperature.

The loss peak at 350 K (Figure 4a) and the modulus variation occur as well upon heating as upon cooling without any hysteresis between the curves, which means that the peak is due to an anelastic relaxation phenomenon. Moreover, it is thermally activated and it was found that the activation enthalpy and the limit relaxation time are characteristic for point defect relaxation [6]. The current interpretation invokes the reorientation of elastic dipoles of the type "oxygen vacancy- yttrium cation" under the influence of the applied stress [6].
In order to determine the origin of the high temperature damping, it is possible to compare the mechanical loss spectrum of the ceramic with the spectra of the constituents: grains and grain boundaries (GB). The comparison in Figure 4b of the high temperature spectra of zirconia poly- and single-crystals shows clearly that the high temperature background is due to GB.

The exponential increase in damping accounts for the appearance of ductility in a hard material. In fact, an exponential increase in $\tan\delta$ can be justified if the anelastic strain does not reach an equilibrium value. In the rheological model of Figure 1b, the spring in parallel with the dashpot would have a stiffness going to zero at high temperature. As a consequence, the anelastic strain is no more limited and creep takes place. In fine grained ceramics, creep has been interpreted as primarily due to GB sliding. As a consequence, the high temperature exponential increase in the mechanical loss would be due to extensive GB sliding.

3. Results obtained in the SAPHIR project.

3.1. Nano-structured Ceramic Matrix Composites (CMCs)

If high temperature plasticity in fine grained ceramics is due to GB sliding, one way to limit GB sliding would be to add extra pinning centers to reinforce the GB triple junctions. This was the goal of reinforcing zirconia with carbon nanotubes (CNTs). 3Y-TZP zirconia was then mixed with multiwalled CNTs and sintered by SPS (Spark Plasma Sintering). Figure 5 shows a fracture surface of one specimen containing 5 wt% CNTs after processing by SPS. One can see that the CNTs are well distributed among the zirconia grains.

Figure 6a shows the variation of mechanical loss ($\tan\delta$) as a function of temperature for CNT/3Y-TZP composites with different amounts of CNTs in comparison with monolithic zirconia. The spectra are characterized by an exponential increase in mechanical loss at high temperature. Clearly, the presence of CNTs shifts the exponential increase at higher temperature, which for 3YSZ/5wt.%CNT seem to start at 1400 K.
Figure 5. High Resolution Scanning Electron Microscopy picture of the composite CNT/3Y-TZP after SPS (fracture surface).

Another interesting point to notice in Figure 6b is the higher shear modulus of 3YSZ/CNTs nanocomposite in comparison with monolithic zirconia in the whole range of test temperature.

![Figure 6](image.png)

Figure 6. a) High temperature mechanical loss and b) shear modulus spectra of CNT/3Y-TZP composites with different CNT content: 1 $\leftrightarrow$ 0 wt%, 2 $\leftrightarrow$ 0.5 wt%, 3 $\leftrightarrow$ 1.5 wt%, 4 $\leftrightarrow$ 3 wt%, 5 $\leftrightarrow$ 5 wt%.

A theoretical model was developed by Lakki [8] to account for the high temperature mechanical loss in fine grained zirconia as due to the relative sliding of grains of hexagonal shape. Taking into account the relative displacement of two grains, which are sliding over an inter-granular layer of thickness $\delta$ and viscosity $\eta$ and the motion of which is limited by a restoring force due to the limiting grains at triple junctions (coefficient $K$), the mechanical loss $\tan\phi$ was found to be:

$$\tan\delta = \frac{G}{d} \cdot \frac{\omega \eta/\delta}{\left(\frac{KG}{d} + K^2\right) + \left(\omega \eta/\delta\right)}$$

(7)

$\tan\delta$ has the form of a peak with a maximum at

$$\omega_p = \frac{\delta}{\eta} \cdot \sqrt{\frac{KG}{d} + K^2}$$

(8)
However, the high temperature mechanical loss spectrum in zirconia does not exhibit a peak, but an exponential increase with temperature (Figures 3 and 6). It is possible to account for this spectrum by considering that the restoring force is reduced at high temperature, where creep takes place. The transition from the peak to the exponential background would be due to the decrease in the restoring force coefficient "K" due to the weakening of the GB triple junctions. As a consequence, reinforcing the triple junctions with nanosized objects such as the CNTs increase the restoring force coefficient "K", which gives rise to a decrease of the high temperature mechanical loss (Figure 6) and of the creep strain in similar stress regime.

Indeed Figure 7 shows the effect of CNTs on the creep strain of zirconia matrix nanocomposites measured in the low stress regime (6 MPa). In general, the curves indicate a typical strain-hardening creep curve, i.e. strain increases and the strain rate decreases with time. Obviously, creep is strongly reduced in the presence of CNTs even with the addition of small amounts of them (0.5 wt.%). With higher amounts of CNT, creep is even suppressed after a certain incubation time. More interestingly, with further addition of CNTs (e.g. 3 or 5 wt% CNTs), after a transient creep during a few minutes, true strain reaches a constant value.

![Figure 7](image)

**Figure 7.** Creep strain in CNT/3Y-TZP composites (X=0 ⇔ 0 wt% CNT, X=0.5 ⇔ 0.5 wt% CNT, X=1.5 ⇔ 1.5 wt% CNT, X=3 ⇔ 3 wt% CNT, X=5 ⇔ 5 wt% CNT) submitted to a compression stress of 6 MPa at 1600 K.

3.2. Nano-structured Metal Matrix Composites (MMCs)

Figure 8 shows the mechanical loss tanδ spectrum and the vibration frequency $f$ of three aluminum matrix composites as measured during thermal cycling (1 K/min) in a torsion pendulum. A2009-SiC is a commercial reference that contains 15%SiC particles with a size of 6 µm. AMC625 is a commercial reference of alloy 6061 with 25%SiC with size of 2 µm. A2009-SiC S was produced in the frame of SAPHIR with alloy 2009 and 15%SiC nanoparticles. In all cases, the mechanical loss increases exponentially with temperature, but new damping peaks appear both in AM625 and A2009-SiC S.
The vibration frequency shows a decreasing trend when temperature increases. As the oscillation frequency is proportional to the square root of shear modulus, the decrease of the frequency is a common behavior. However, the comparison of the reinforced alloys 2009 is particularly interesting since with the same matrix a higher damping level is obtained in the nanostructured materials. Moreover, an increase of the oscillation frequency is clearly observed up to 500 K. The same trends are observed in AMC625 but the modulus increase should be attributed to the higher particle content. The exponential increase in mechanical loss at high temperature is related to a bad creep resistance of the material, because the anelastic or microplastic strain has no limit. On the other hand, damping mechanisms are positive factors for improving toughness. As a mechanical loss peak is associated with a limited motion of structural defects, it cannot be associated with the onset of creep. It accounts for the ability of the material to dissipate locally a part of the vibration energy and hence to improve toughness by crack propagation blunting. In the present case, the higher level of the mechanical loss in AMC625 is due to a higher peak at about 450K and not to a higher exponential background at 650 K (Figure 8). In the nanostructured composite A2009-15%SiC S, two damping peaks are found over an exponential background quite similar to that of A2009-15%SiC. As a consequence, one can suppose that A2009-15%SiC S new composite, which has a higher modulus and higher damping capacity than A 2009–15% SiC, exhibits a higher stiffness and higher toughness with a similar refractory character at least up to 500 K. Instead, AMC625 should exhibit good properties over a wider range of temperature but the higher content in SiC particles may lead to a higher brittleness.

ODS steels to be used for pelleting nuclear fuel for next generation of fission power plants has been analysed by mechanical spectroscopy. A traditional steel F-70 and a new one processed by CEA (10078) both with 18%Cr were studied. The mechanical loss spectra show a very different behavior (Figure 9). The new one has a high damping peak at 860 K (590 °C) just visible in F-70. Moreover, the damping background at high temperature is much lower in the CEA steel. This difference let us envisage that the new process could lead to a tough and refractory steel in the domain of nuclear application from 600 °C to 900 °C (900 -1200 K).
3.3. Nano-structured Polymer Matrix Composites (PMCs)

Mechanical spectroscopy has been used to quantify the improvement of the mechanical properties of polymer based materials by the introduction of nanoparticles. For example, the mechanical loss and shear modulus spectra of Acrylonitrile-Butadiene-Styrene (ABS) are shown in Figure 10a. We notice the typical peaks of polymer spectra each one characterizing the onset of a molecular motion [1]. At low temperature, we find the $\beta$ relaxation that is attributed to the rotation of side radicals or groups along the polymer chain and, at high temperature, the $\alpha$ relaxation that marks the glass transition of the polymer. At the glass transition, the elastic modulus drops to almost zero.

In the second step of this study, we have analysed the spectra of polymers reinforced with nanoparticles or nanotubes. Composite samples with ABS matrix and CNT (Arkema) reinforcement were processed by CRP (Centro Ricerche Plast-Optica, Amaro, Italy). The CNT additions were 3%, 7% and 15%. In Figure 10b, the spectra around the $\alpha$ transition are shown. We notice that the glassy transition is broadened by the presence of CNT. Moreover, it is slightly shifted to higher temperatures. The analysis of the microstructure shows that the $\alpha$-transition occurs in the Styrene-Acrylonitrile (SAN) phase. Therefore, the peak broadening is related to the interaction of CNT with such phase.
CNT also produce a significant stiffening of the material reducing flow in the viscous phase. Such behavior can be seen by the observation of the samples heated up to 430 K in the pendulum. The pure ABS sample flows while the CNT containing sample remains stable (Figure 11).

4. Conclusions.
Mechanical spectroscopy has shown that most of the new nano-structured composites, which have been developed within the SAPHIR project, exhibit better thermo-mechanical behavior than the classical materials. For instance, it has been observed that reinforcing fine grained zirconia with multiwall carbon nanotubes (MWCNTs) improves simultaneously the creep resistance and the toughness of these ceramics [9]. In aluminum matrix composites, nanosized SiC reinforcements give rise to a simultaneous increase of the elastic modulus and of the damping level from room temperature up to 500 K that indicates a higher stiffness and a higher toughness of these MMCs. The introduction of MWCNTs in a polymer matrix such as ABS significantly improves the thermal stability of the polymer, as it can be seen by the temperature broadening of the alpha relaxation peak (widening of temperature range the glass transition).

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References
[1] Mechanical Spectroscopy Q1 2001, Schaller R, Fantozzi G and Gremaud G, Eds, 2001 Mater. Sci. Forum 366-368.
[2] Nowick A S and Berry B S 1972 Anelastic Relaxation in Crystalline Solids, (New York: Academic Press)
[3] Schaller R, Daraktchiev M and Testu S 2004 Mater. Sci. Eng. A 387-389 687.
[4] Schaller R 2000 J. Alloys and Compounds 310 7.
[5] Mayencourt C and Schaller R 1998 Acta Mater. 46 6103.
[6] Weller M 1994 Journal of Alloys and Compounds 211/212 66.
[7] Schaller R 2006 Mater. Sci. Eng. A 442 423.
[8] Lakki A, Schaller R, Nauer M and Carry C 1993 Acta Metall. Mater. 41 2845.
[9] Mazaheri M, Mari D, Schaller R, Bonnefont G. and Fantozzi. G to be published in the J. Eur. Ceram. Soc.