Fundamentals of the Thermomechanical Analysis in Materials Science

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1. Introduction

Whenever a sample of material is to be studied, one of the easiest tests to perform is to heat it. The observation of the behavior of the sample and the quantitative measurement of the changes in temperature can yield a lot of useful information. The study of the relationship between a sample property and its temperature as the sample is heated or cooled in a controlled manner is commonly referred to Thermal analysis (TA). Several methods are used – these are distinguished from one another by the property which is measured. A summary of some of methods are presented in Table 1. One of them is Thermomechanical Analysis (TMA). The method is defined by the International Confederation for Thermal Analysis and Calorimetry (ICTAC) [1] as a technique where the deformation of the sample is measured under constant load. This is realized by measuring dimensional changes of solids, liquids or pasty materials as a function of temperature and time under a defined mechanical forces. The result of TMA measurements is a curve showing the change of the sample length versus temperature and time. It is powerful tool used in the analytical laboratories. It can hereby provide valuable insight into the composition, phase changes, structure, sintering steps or softening which can occur in addition to thermal expansion, production conditions or application possibilities for various materials. Typical domains include plastics and elastomers, paints and dyes, composite materials, adhesives, films and fibers, ceramics, glass, metals, and composite materials. The measurements can be carried out by the number of different probe configurations. Depending on the applied load experiments may be done in compression, tension, shear, torsion, penetration or some bending mode as shown in Figure 1. The choice of the measurements mode depends on the studied properties, shape of the sample and/or its application.

The most usual modes of measurements are compression (for self-supporting samples) and tension (for thin films and fibers). These modes are used mainly in order to determine the phase transformation temperatures and the thermal expansion coefficients. For example, a crystalline materials may exist in a number of polymorphic forms which are stable at different temperatures. The transition between crystal structures is usually accompanied by the change in density and thermal expansion. It is manifested in the TMA measurements by a step or by the variation of the slope of relative changes of the samples length (dL/L_0) at temperature T, ($dL/L_0 = f(T)$).

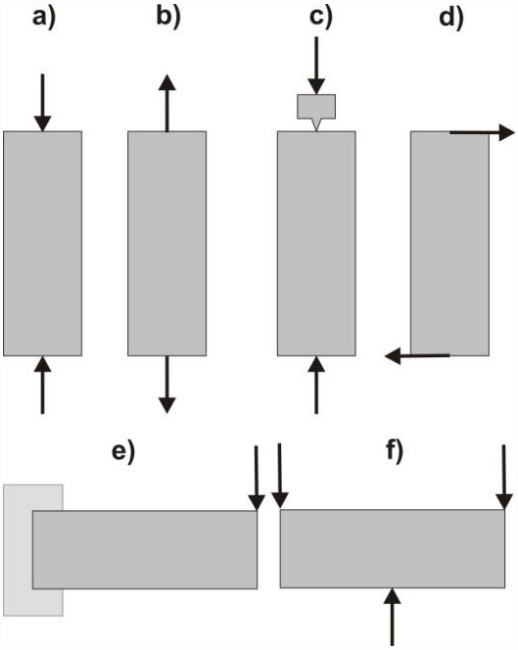

Figure 1. Common mechanical deformation modes in TMA: a) compression, b) tension, c) penetration, d) shear, e) bending, f) three point bending [2].

The slope of the curve is named coefficient of the linear thermal expansion and may be recorded as the mean value $\bar{\alpha}(\Delta T)$ or by differential value $\alpha(\Delta T)$. The $\bar{\alpha}(\Delta T)$ and $\alpha(\Delta T)$ coefficients of linear thermal expansion are derived as follows:

$$\bar{\alpha}(\Delta T) = \frac{1}{l_0} \cdot \frac{l_2 - l_1}{T_2 - T_1} = \frac{1}{l_0} \cdot \frac{\Delta l}{\Delta T}$$

$$\alpha(\Delta T) = \frac{l}{l_0} \cdot \frac{dl}{dT}$$

where l_o is initial length, l_1 , l_2 are length in temperature T_1 and T_2 respectively.

Measurements of the thermal expansion coefficients are useful in assessing the compatibility of different materials for fabrication into components. Mismatches in their behavior can caused stresses to build up when temperature changes occur, resulting in eventual weakening and failure of the structure. Linear thermal expansion coefficient and other materials properties also depend on applied leads.

2. Measuring Principle

A schematic diagram of the typical instrument is shown in Figure 2. The sample is placed in the chamber where the temperature is controlled by the thermocouple placed close to the sample. The measurements are performed in the protective atmosphere of inert gases like: nitrogen, helium or argon but also the other gases could be used i.e. air, carbon monoxide, hydrogen. Because of the relatively large mass of the sample the applied heating and cooling rates are usually slow. The rate of 5°C/ min is usually the maximum recommended value for good temperature equilibration across the specimen.

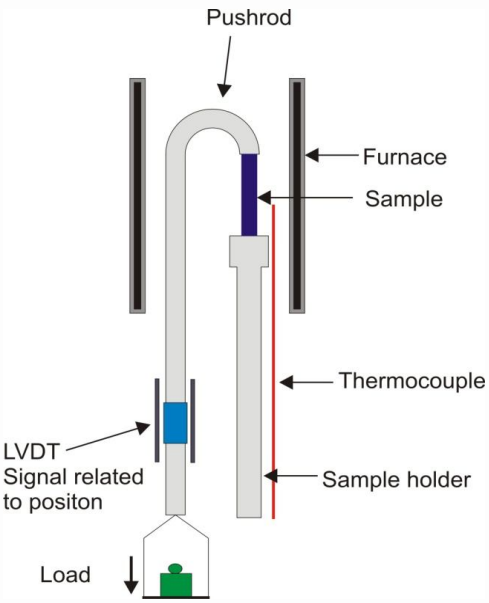

Figure 2. Schematic diagram of a thermomechanical analyzer.

The dimensional changes of the sample relative to the holder appearing during heating or cooling are transmitted via pushrod to the highly precise inductive transducer (LVDT) sensor. The construction of the pushrod and sample holder depends on the mod of the measurements. The most commercial instruments are supplied with a variety of probes for different applications. Figure 3 presents the examples of the holding devices taken from the TMA 402 F1 Hyperion, NETZSCH [3]. Every displacement of the pushrod is transformed into analog signal by the LVDT and in the next converted to digital form then recorded in the PC system and finally presented by the software as a dimensional change versus time or temperature.

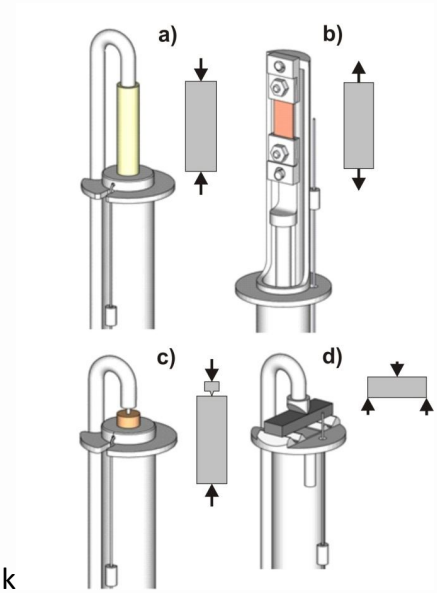

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Figure 3. Holding devices for a) compression , b) tension, c) penetration, and d) 3-point bending [3].

3. Application Examples

An examples of measurements of the length change for the cylindrical sample of Ni-Sn alloy in compression mode under 0.04N applied loads and heating rate 5°C min-1 is shown in Figure 4. This example illustrates the determination of phase transformation temperatures (287.8 , 949.0 °C) by TMA analyses indicating by inflections ranges in the presented curve.

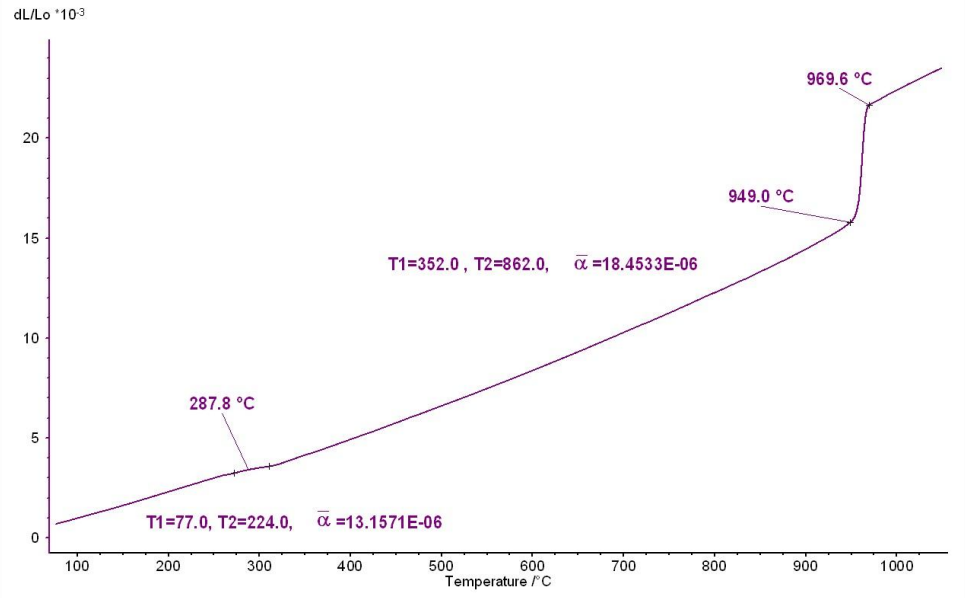

Figure 4. Plots of the length change for the cylindrical sample of Ni-Sn alloy under 0.04N applied load and heating rate 5°C min-1, under inert gas helium (compression mode).

TMA is very often used to measure glass transition, based on changes in coefficient of thermal expansion which results as the free volume of the material changes at the glass transition. Figure 5 shows T_g of amorphous metal ribbons heated at 5°C/min under 2N and 0.05 force loading. T_g is defined as the onset of change in rate of the expansion (slope) at 423°C and as the shrinkage at 420°C on the second curve.

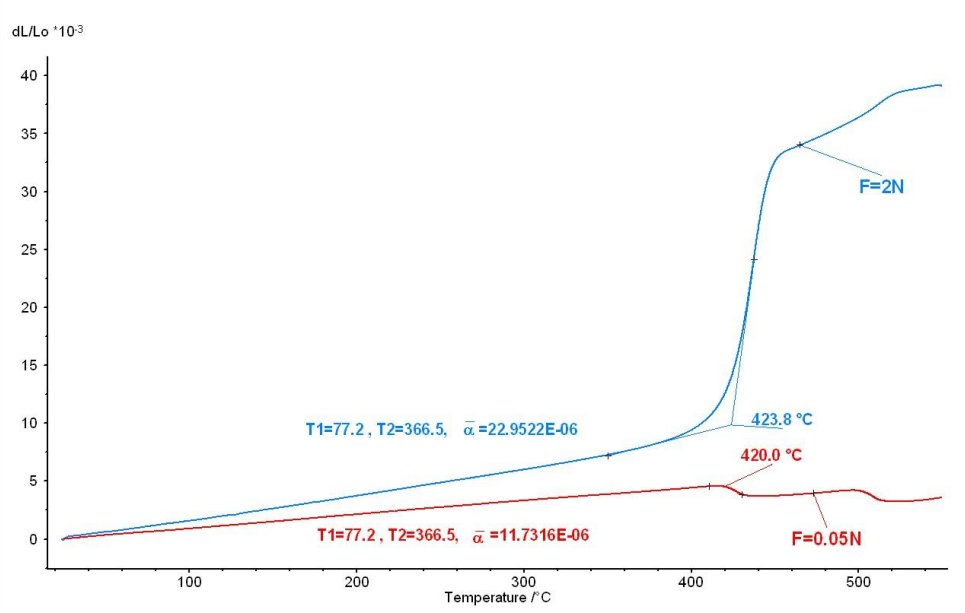

Figure 5. Plots of change in the length for two the amorphous metal ribbons under different applied loads F=2N and F=0.05N. Heating rate 5°C min-1 under helium, inert gas (tension mode).

A fundamental property of different kinds of materials like metals or plastics is their melting point. It can be determined by DSC method but only in temperature where the heat consumption of the crystalline melting takes place. It also can be determined by the use of the thermo mechanical analyzer to identify where the sample transforms from rigid body to soft or flexible i.e. in that point where thedramatic decrease in modulus taken place and then sample deforms, even under low forces. The result of the melting temperature determination for high temperature metallic solders are present on figure 6.

Thermomechanical analysis can by also carried out in isothermal conditions for example to test polymers behavior under pressure (Figure 7). The extent to which the elastic properties of a seal remain intact after being subjected to the constant load of longer duration is very important. To test this, an elastomer seal was loaded with the force of 3 N and then relieved to 5 mN. Following a 40-hour load time, 21% compression was observed. After a 30-minute relief period, the compression had reversed by 16.2%; after 60 min, by 16.8%. The visco-elastic properties of the elastomer were such that the sample did not return to its original length even after 30 hours [4] (measurement with TMA 402 F1 Hyperion®).

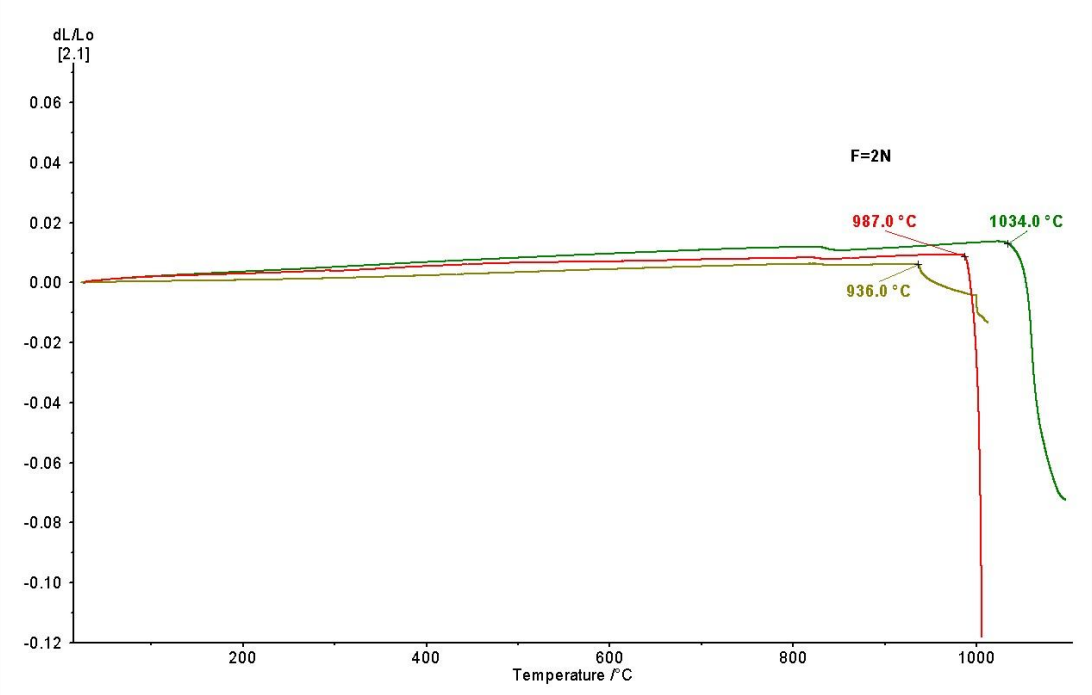

Figure 6. Softening point of a high temperature solders alloys (penetration mode).

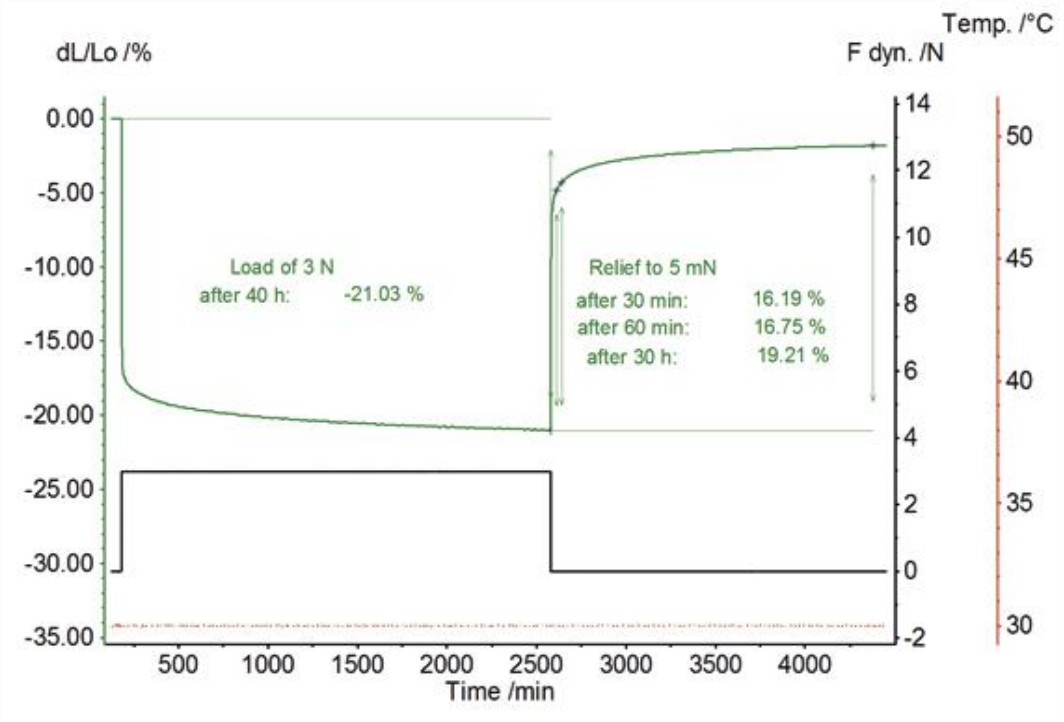

Figure 7. Polymers behavior under pressure during isothermal test (compression mode) [3]

Moreover the TMA is useful and vital in sintering process. The principal process of the ceramics bonding into solid pieces is sintering and this result in shrinkage. Using TMA with either constant rate of heating or isothermally , provides a method of analyzing this process. Figure 8 shows the measurement of an aluminum titanate in range from rum temperature to 1450°C with a subsequent isothermal line at 1450°C of 7 hours. During the heating, shrinkage of 12.7% is observed.

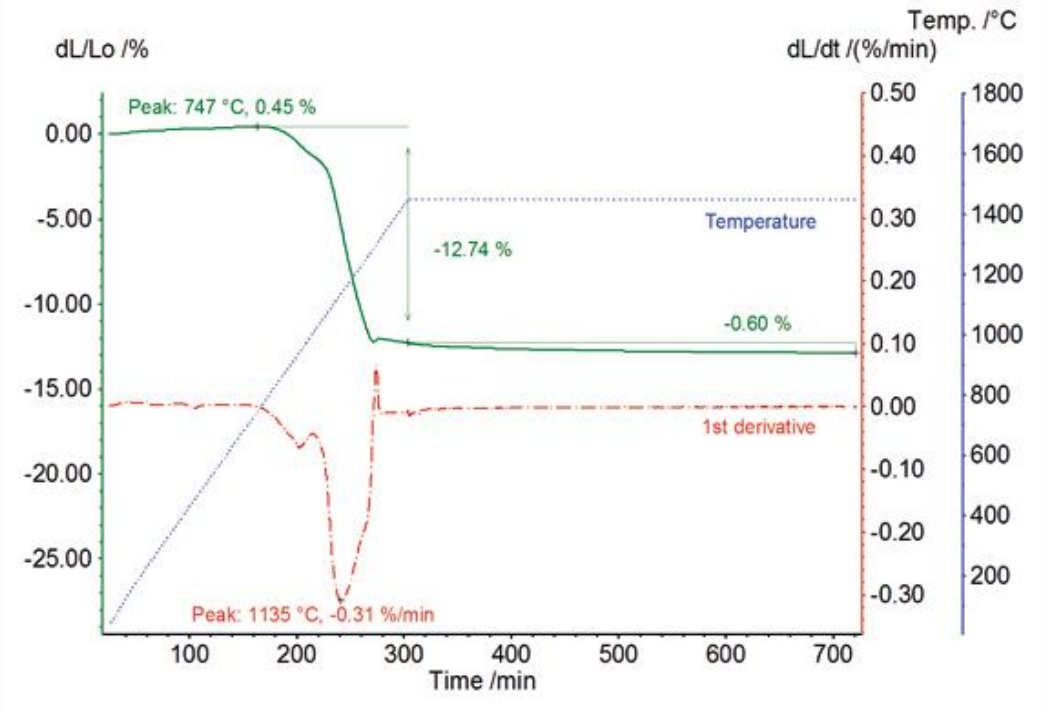

Figure 8. Aluminum Titanate – Sintering [3]

4. References

1. International Confederation for Thermal Analysis and Calorimetry (ICTAC) nomenclature of thermal analysis (IUPAC Recommendations 2014)

2. Principles of Thermal Analysis and Calorimetry Haines, P. J. (Ed.), Royal Society of Chemistry, Cambridge (2002) .

2. Instrument manuals for TMA 402 F1 Hyperion, NETZSCH

3. Web site: www.netzsch-thermal-analysis.com

Table 1. Technique exists for each property or physical quantity that is measured versus temperature [1].

Property or physical quantity	Technique	Technique acronym	Notes
Heat	Scanning calorimetry		
Temperature	Thermometry		May also be described as heating or cooling curves.
Temperature difference	Differential thermal analysis	DTA	A technique where the temperature difference between a sample and a reference material is measured.
Heat flow rate difference	Differential scanning calorimetry	DSC	A technique where the difference between heat flow rates into a sample and a reference material is measured.
Mass	Thermogravimetry or Thermogravimetric analysis	TG TGA	In any work where a confusion may arise between TG and Tg (the glass transition temperature), the abbreviation TGA or the full term "thermogravimetry" should be used.
Dimensional and mechanical properties	Dynamic mechanical analysis	DMA	Moduli (storage/loss) are determined.
	Thermomechanical analysis	TMA	Deformations, and dimensions are measured.
	Thermodilatometry	TD	Dimensions are measured.
Electrical properties	Dielectric thermal analysis	DEA	Dielectric constant/dielectric loss is measured.
	Thermally stimulated current	TSC	Current is measured.
Magnetic properties	Thermomagnetometry		Often combined with TGA.
Gas flow	Evolved gas analysis	EGA	The nature and/or amount of gas/vapour are determined.
	Emanation thermal analysis	ETA	Trapped radioactive gas within the sample is released and measured.
Pressure	Thermomanometry Thermobarometry		Evolution of gas is detected by pressure change Pressure exerted by a dense sample on the walls of a constant volume cell is studied.
Optical properties	Thermoptometry		A family of techniques in which an optical characteristic or property of a sample is studied.
	Thermoluminescence	TL	Emitted light measured
Acoustic properties	Thermosonimetry or Thermoacoustimetry		Techniques where the sound emitted (sonimetry) or absorbed (acoustimetry) by the sample is studied.
Structure	Thermodiffractometry Thermospectrometry		Techniques where the compositional or chemical nature of the sample are studied.