The application of thermal analysis in the study of metallic materials

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1. Introduction

The first commercial TGA equipment appeared in 1945 and was followed by DTA in 1960 and DSC in 1964. *The Journal of Thermal Analysis* appeared for the first time in 1969 and *Thermochimica Acta* came out the following year.

In the seventies, when thermal analysis methods started to be generally applied, major advancements in scientific research related to metallic materials' behaviour had already occurred. This was especially true in the case of alloys with greater industrial demand, such as steel, or alloys with greater future expectations, such as light alloys and mainly aluminum alloys. In the first half of the past century, famous metallurguists such as Bain, Davenport, Grossmann, and Jominy, amongst others, carried out a very important task. These scientists, along with institutions like the A.S.M. (American Society for Metals) and the IRSID in France, led to the creation of the Atlas of T.T.T. and C.C.T. curves of commercial steels, applying techniques like dilatometry, which measures the dimensional variation of the tested sample according to the temperature, and metallography, which freezes the structure after an isothermic period of a different duration at various temperatures.

All this led to thermal analysis methods not initially being applied to metallic materials, but to other materials that were being discovered and were practically unknown in their properties and characteristics. This was due to the limitations of the methods used, especially with respect to the range of working temperatures, whose application to metallic materials was not very useful at that time.

Nevertheless, metallic materials, upon conditioning their microstructure not only by temperature, but also by conditions of the process (speed of heating and cooling), could be treated with these analysis methods. As a result, fusion temperatures and the latent heat of fusion, allotropic transformations, transformations with a phase change in solid state in which diffusive phenomena can intervene, equilibrium diagrams, transformation kinetics, changes in magnetic behaviour, behaviour with respect to oxidation at high temperatures, the coefficient variation of thermal expansion, the variation of specific heat, and thermal stability could be determined using these methods. In general, any process that could be activated thermally can be studied with DSC. In addition, it can characterise transformation kinetics. Similarly, all those processes involving a modification in the mechanical properties can be studied using DMA or TMA. Examples of these phenomena include the precipitation processes of intermetallic compounds in some alloys that involve amplification in the elastic modulus and phase transformations.

Some specific applications of thermal analysis methods on metallic materials are pointed out below.

2.   Shape memory materials

There are metallic materials known as shape memory materials because they present the special feature of undergoing a transformation in the solid state known as martensitic. It generally occurs at low temperatures and diffusive phenomena do not intervene. When these materials are plastically deformed at a temperature below the final temperature of martensitic transformation, they can later recuperate the original shape by heating the material above the final temperature of the reversible transformation.

Due to their shape memory effect, their superelastic distribution, their absorption capacity, their change of resistance, and their good mechanical properties, shape memory materials tend to be used as fire detectors, muscles in robotics, mechanical sensors (for example, for the opening of windows for ventilation), and dental prosthesis, amongst other uses.

In the past years, different works have appeared in which the application of the DSC method is used for the determination of characteristic temperatures and of enthalpy changes associated with endothermic and exothermic processes that occur during the controlled heating and cooling of these types of materials [1-7].
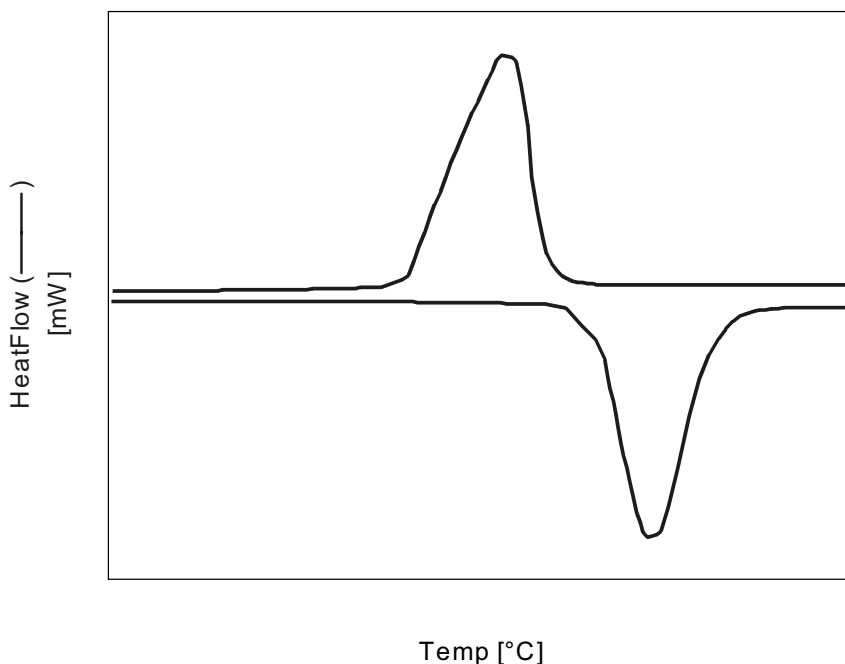

Figure 1. DSC curve showing the martensitic transition reversibility in a shape memory alloy
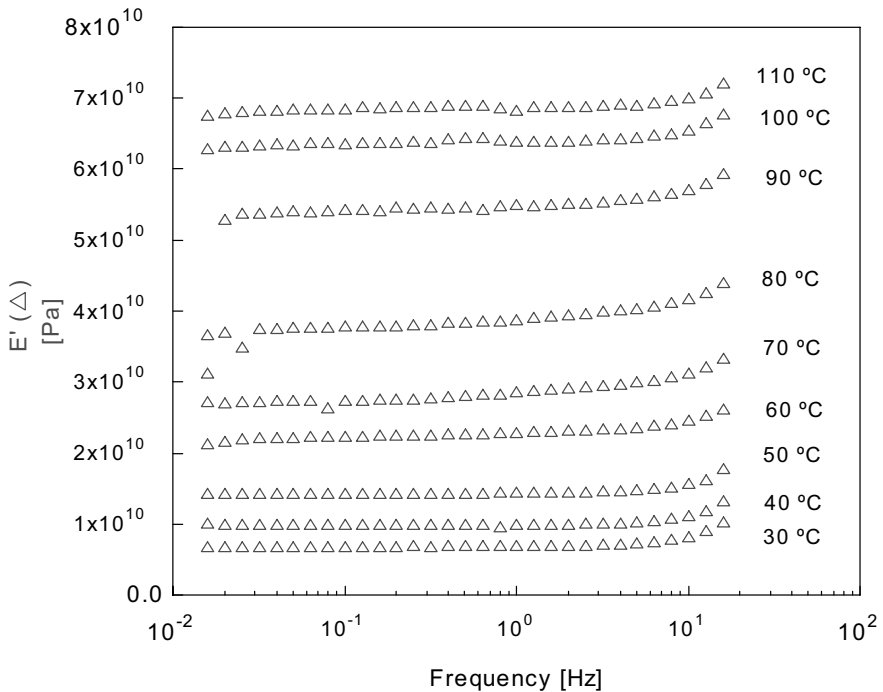
Figure 2- Determination of the martensitic transition temperature with DMA.
According to reference [15]

The transition temperature for this class of alloys can also be determined employing DMA methods. In Figure 2, the elastic modulus obtained for an equiatomic alloy of nickel and titanium according to the frequency of nine different temperatures is shown. The martensitic transition temperature can be determined observing the separation between curves which increase around that temperature. In addition, it is possible to observe how the curve for the transition temperature presents a greater slope than the rest, which indicates the modulus's dependence on the frequency is increased for the martensitic transition temperature.

A third way to study martensitic transformation temperatures of shape memory alloys is through the use of TMA. In Figure 3, the deformation that is tested on a wire of the same alloy is shown. In the previous example, it was deformed according to time when the temperature varied and when it was subjected to a constant force.
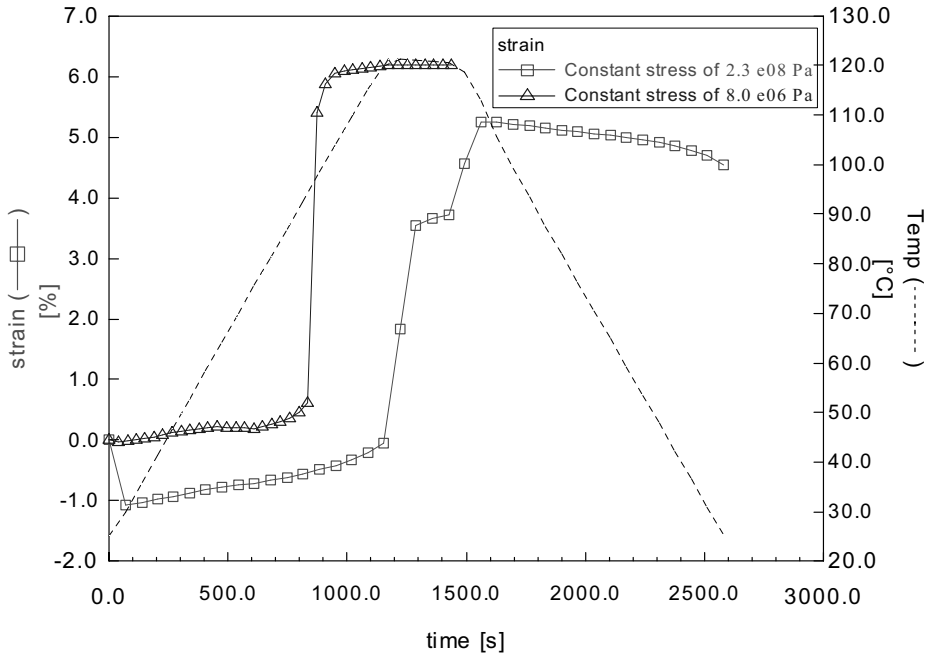
Figure 3. Determination of the martensitic transformation temperature with TMA.
According to reference [15]

In Figure 3 a sharp increase in the elastic modulus's value is observed when the transformation temperature is reached. As this transformation temperature shifts towards higher values, the applied force increases from 8.0 MPa to 2300 MPa.

3. Determination of the progress of metal and alloy solidification.

If the alloy's solidification is studied using the DSC curve, as in the example of an alloy of lead-tin, and if the solidification's interval is centred, the evolution of the liquid phase percentage according to the temperature can be traced. [8-9].
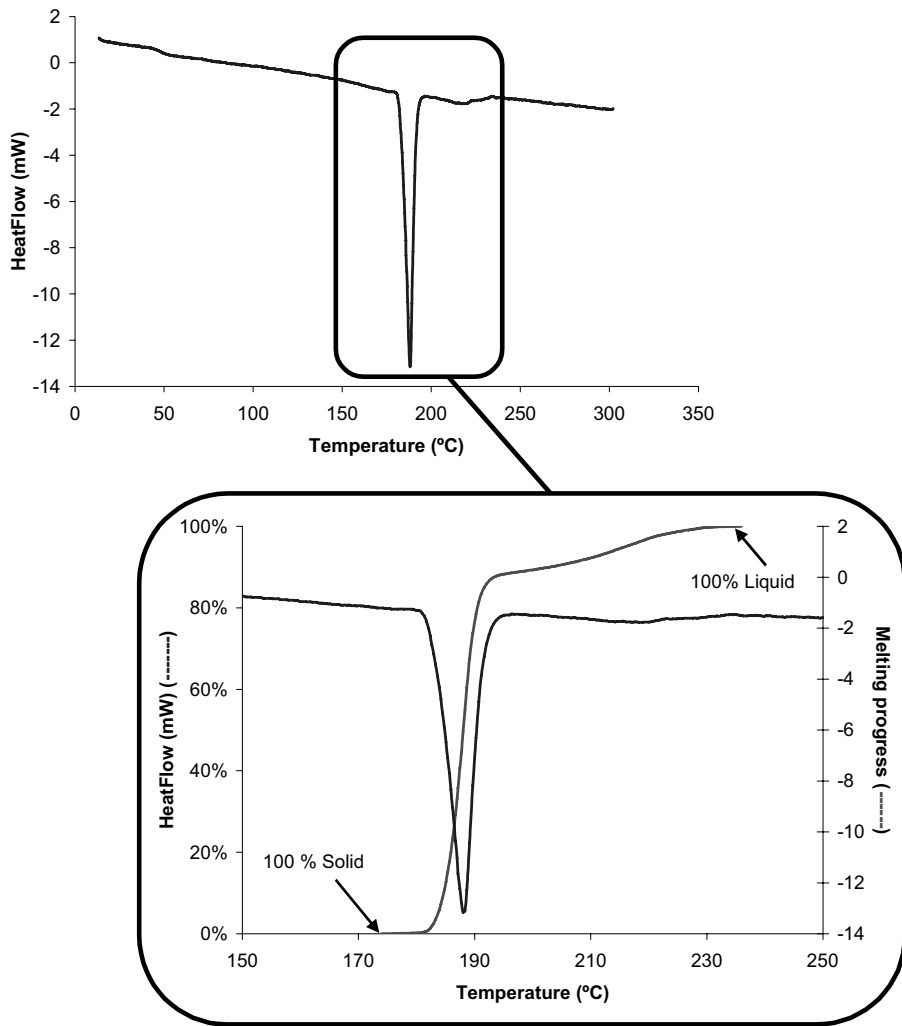
Figure 4. DSC curve, endothermic fusion and variation of the liquid phase percentage determined using the Borchardt and Daniels method [16]

4. Determination of equilibrium diagrams.

If we obtain the curves for different alloys of binary [10] or ternary [11] systems with DSC, the *liquidus* and *solidus* temperatures as well as those temperatures corresponding to transformations in solid states can be determined. These curves are created from all the information obtained in the analysis of the same temperatures with respect to the appropriate equilibrium diagrams.

In the following example, we notice how the diagram structure of the appropriate phase corresponding to a lead-tin system is carried out step by step. From

the DSC curves obtained during the solidification, the appropriate temperatures at the beginning of solidification (point of the *liquidus* line) and the eutectic transformation's temperature for alloys with different proportions of lead and tin are determined.
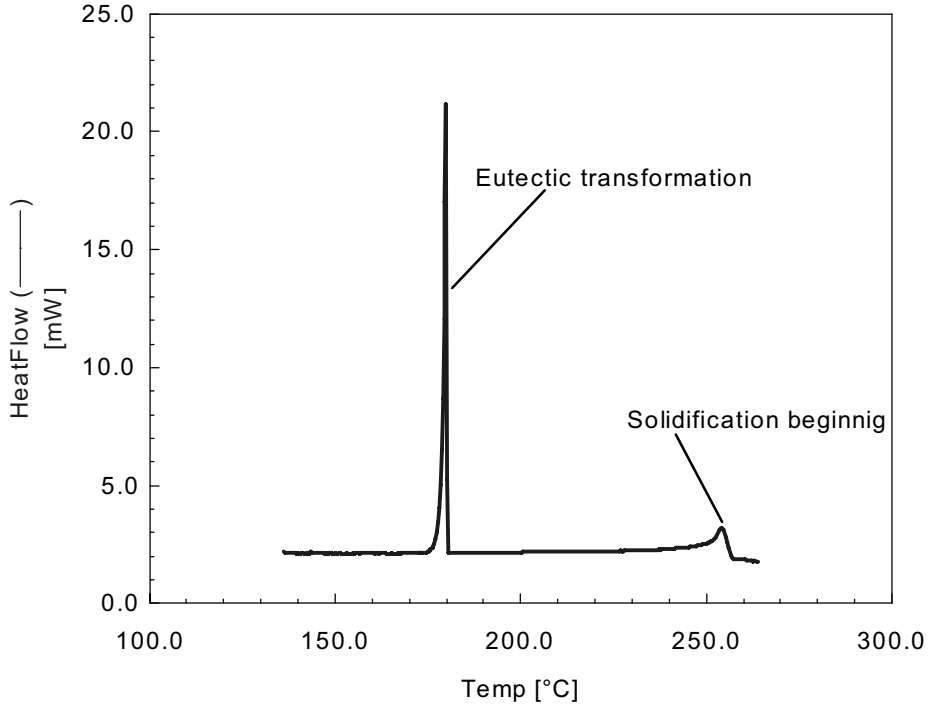

Figure 5. DSC curve obtained during the solidification of an alloy with 30% tin and 70% lead

If points for the different alloys of lead and tin are determined, it is possible to begin the construction of the phase diagram, as can be seen in Figure 6. In this figure, the alloy's composition with respect to the temperature is shown. We are able to see each one of the DCS curves obtained for the different alloys with their liquidus and solidus lines' appropriate points. We also can see the points of fusion of the two metals in pure state and the way of tracing the lines of the phase diagram.
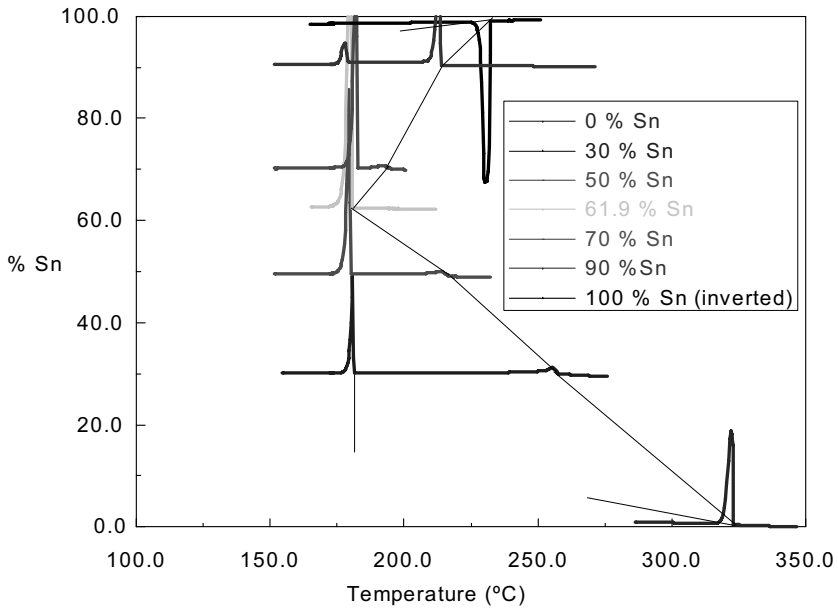
Figure 6. Pb-Sn phases diagram construction

In order to establish the point of maximum solubility and the eutectic alloy's composition, should it not be known, the Tamman triangle, which shows the appropriate peak's area for the eutectic transformation, is constructed. For those alloys that are tested on the basis of the alloy's composition, see Figure 7.
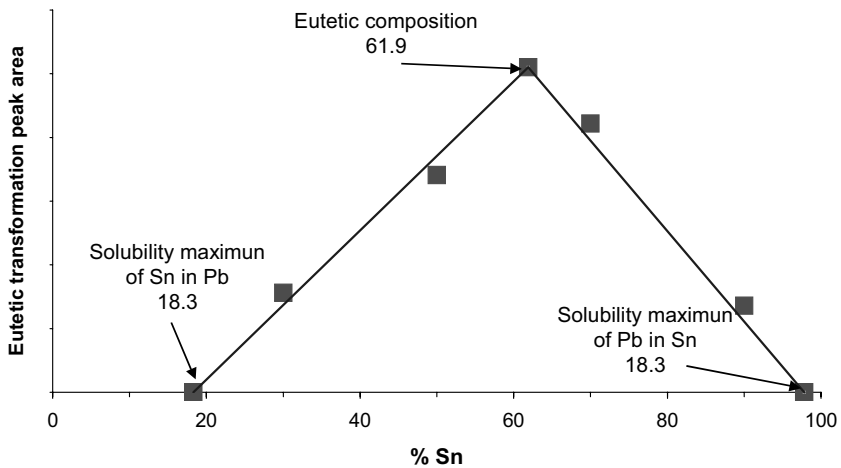

Figure 7. Determination of the points of maximum solubility and of the eutectic composition for the Pb-Sn system

5. Measurement of heat capacity.

Using DSC, the variation of the heat flow with the temperature of the tested sample is obtained. The results are compared with the base line of synthetic sapphire that is taken as normal specific heat and allows the apparatus's software to determine the specific heat's variation with the temperature [12-13].
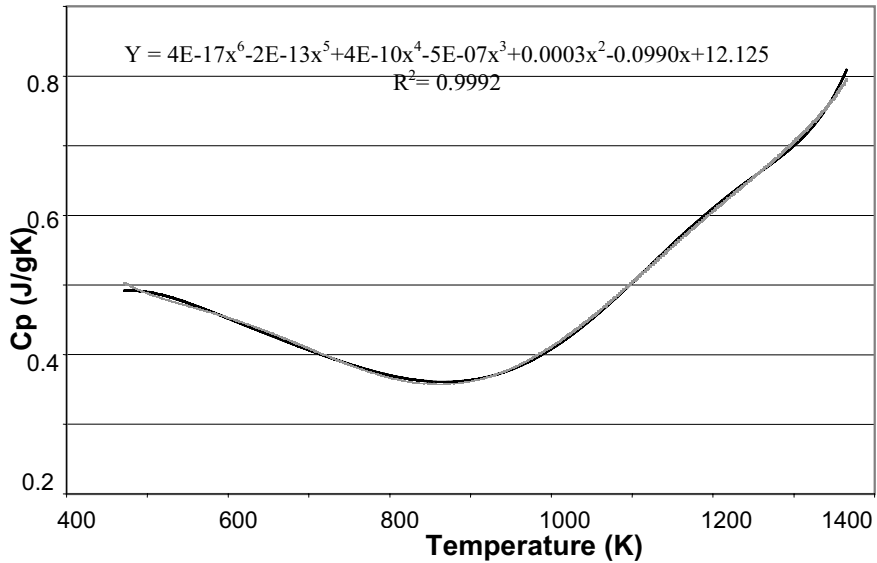

$$Y = 4E-17x^6-2E-13x^5+4E-10x^4-5E-07x^3+0.0003x^2-0.0990x+12.125$$
$$R^2= 0.9992$$

Figure 8. Variation of Cp with the temperature in a nickel-based superalloy. According to reference [13-14]

6. Transition temperatures: magnetic change or Curie's temperature, allotropic transformations, fusion temperature, transformation with phase change in solid state.

Using DSC, all these temperatures as well as the energy associated with the appropriate transformations can be detected.
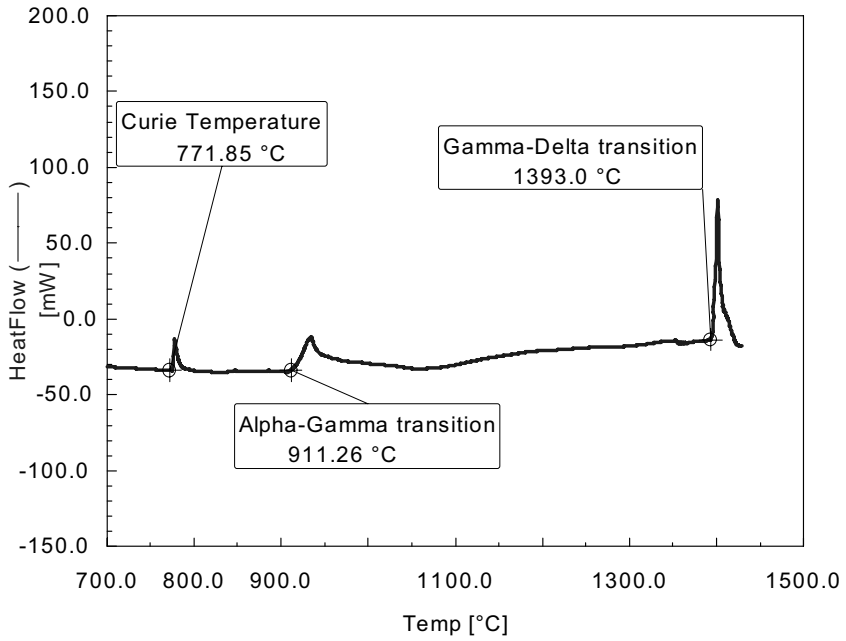
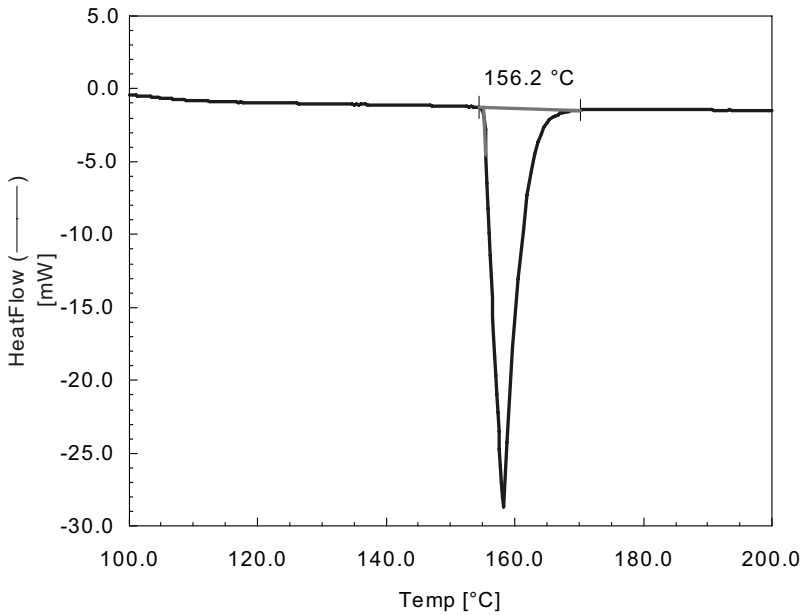*Figure 9. Allotropic transformations of pure Fe*

Figure 10. Determination of the fusion temperature of pure indium

In addition, by means of TMA, it can be suggested that dimensional change, either contraction or expansion, is associated with crystalline structure changes in transformations with phase changes in the solid state.
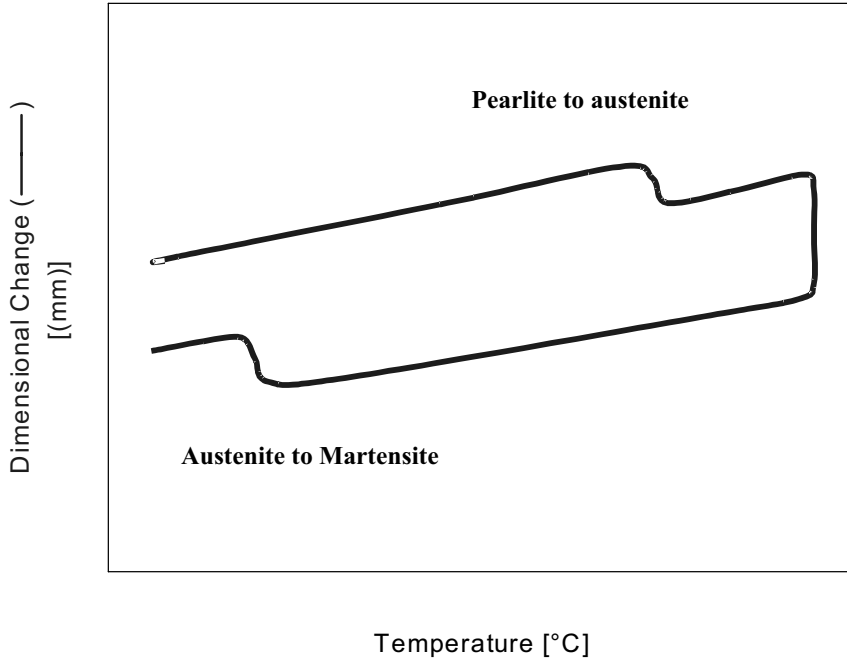

Fig. 11. Dimensional changes that are produced in steel subjected to heating and then to cooling

7. Behaviour with respect to oxidation at high temperatures

Using TGA and regulating the nature and atmospheric pressure in the thermobalance's interior, the material's behaviour with respect to the time periods at various temperatures can be measured.
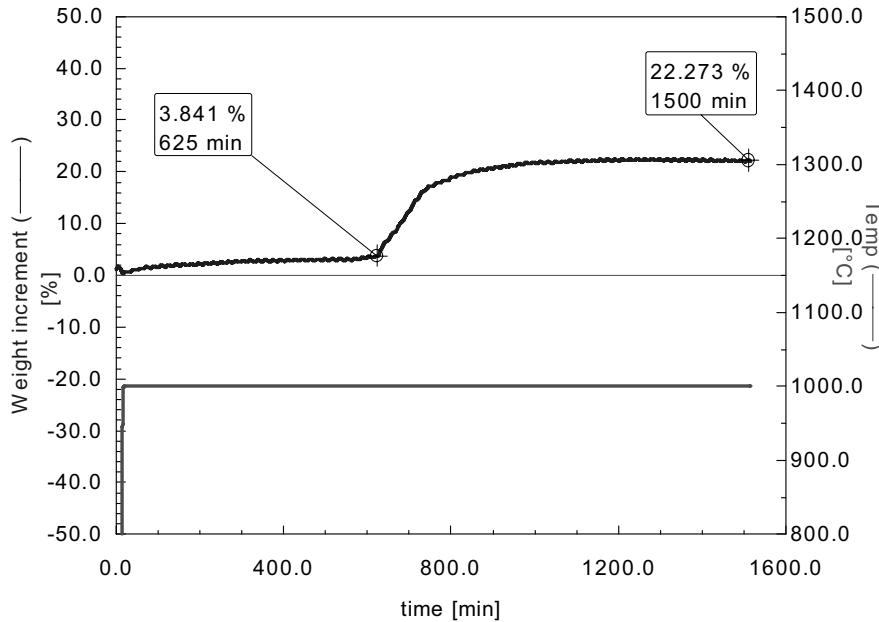
Fig. 12. Oxidation at high temperatures of stainless steel in the air's atmosphere

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