# The Differential Scanning Calorimetry in the Study of Thermal Treatments of Al and Mg Alloys

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## ABSTRACT

*Studies are reported of phase transformations in some Al and Mg based alloys submitted to heat treatments. A description is given of the use of Differential Scanning Calorimetry (DSC) that, by monitoring the sequence of energy emission or absorption on heating, enables to identify temperature ranges suitable for conventional or innovative thermal treatments aimed to increase some mechanical properties. Microhardness tests made in order to assess the effectiveness of the thermal treatments are reported. A mechanism of secondary precipitation is proposed to explain the hardness increase with respect to conventional treatments of artificial ageing.*

## RIASSUNTO

Sono riportati alcuni esempi di studi sulle trasformazioni di fase che avvengono in leghe di alluminio e in leghe di magnesio trattate termicamente. Vengono riportate misure di calorimetria differenziale a scansione (DSC) ottenute monitorando la sequenza di emissione o assorbimento di energia al variare della temperatura. I relativi risultati consentono di identificare campi di temperatura entro i quali conviene effettuare trattamenti termici, convenzionali e/o innovativi, per migliorare le proprietà meccaniche. La valutazione dell?efficacia del trattamento termico poggia su misure di microdurezza. Viene proposto un meccanismo di precipitazione secondaria per spiegare l?aumento di durezza ottenibile mediante un trattamento di invecchiamento artificiale non convenzionale.

## INTRODUCTION

The need for the highest possible performance/weight ratio in the transport industry has favoured the use of light Al or Mg alloys. Commercially available Al alloys are widely used in several sectors; a variety of compositions allow to satisfy different specific requirements. Mg alloys are currently used in the fields of aeronautics and automotive due to their good formability and mechanical properties. Nevertheless, only recently magnesium alloys have become the object of in-depth studies making it possible to overcome some technological problems and to extend their use to a greater number of fields which, however, remain limited because of the relatively high cost of magnesium.

Renewed attention has been given to the study of thermal treatments since they modify the alloy microstructure, strongly affecting the mechanical performance. Starting from the oversaturated solid solution, commonly used to prepare the alloys, thermal treatments lead to the formation of different metastable phases which are the main causes of the improvement of mechanical properties through the process of precipitation hardening.

The hardness increase [1] is utilized as a criterion for assessing the effectiveness of the non conventional, multistage thermal treatments investigated in the present research. Two multistage treatments (whose effectiveness depends on the composition of the alloy) are explored. The first provides an initial treatment at temperatures close to those commonly used to form the phase or the phases combination that leads to the best mechanical properties (T6 treatment). After this first annealing, there may be a certain degree of solute atoms oversaturation: this is not sufficient to reform the main hardening phases, but it can form other intermediate metastable phases. A successive treatment at lower temperatures is able to promote the formation of further precipitates that add their hardening effect to the ones formed during the first stage. This phenomenon is known as secondary precipitation.

The second multistage treatment involves a first ageing stage at a relatively low temperature to form a fine dispersion of precursor precipitates and a second ageing at higher temperature (similar to the T6 treatment) to promote the formation of the main hardening phases. The latter can

nucleate more easily on the precipitates formed during the first stage, also maintaining the finely dispersed distribution typical of the precursors.
The need to monitor the microstructural transformations arises following thermal treatments in a complete and reproducible way, overcoming the often empirical choice of times and temperatures. To this aim, the DSC has proved to be [2-5] a powerful investigation method. By detecting the heat variations due to the phase transformations, the technique is able to identify the temperature ranges in which they occur. Combined with techniques of direct analysis like TEM, DSC allows a complete characterisation of the microstructural evolution. Combined with microhardness measurements as well, the calorimetric analysis makes it possible to correlate the microstructural evolution with the trend of some mechanical properties, thus identifying critical temperatures and allowing the design of optimised thermal treatments for different compositions.
The aim of this work is to show how the combined use of calorimetric techniques and microhardness is a very helpful starting point for the study of alloys in which the precipitation hardening takes place. In this way, it is possible, from a technological point of view, to optimise thermal treatments and to design new ones starting from reliable and reproducible data. The examples reported in this paper are part of a series produced by the authors in collaboration with other researchers, aimed to a full structural characterization of alloys of different composition involving several complementary investigation techniques [6-17]

## MATERIALS AND METHODS

Table 1 reports the chemical compositions of three heat treatable hardenable alloys. The 7020 is a typical aluminum alloy for extrusion, used in different sectors as a structural material. The alloys WE43 and QE22 are magnesium alloys with rare earth (RE) elements: they offer good opportunities for aeronautical uses, combining lightness with good mechanical characteristics, in particular good creep resistance.
Discs 20 mm in diameter about 1.5 mm thick were obtained from the original homogeneized bars. From these discs smaller discs of about 5 mm in diameter were obtained by punching. These smaller discs have been solution treated at the temperatures and for the times reported in Table 2, then quenched in water (w.q.) at room temperature. The solution treatment was carried out in a vertical furnace, the samples being sealed in pyrex vials. The successive thermal treatments were performed in an air ventilated furnace or in a resistance furnace depending on the temperature. For all the samples, the small superficial oxide layer was removed by a light mechanical polishing.
The calorimetric analysis was carried out by a TA® 2010 cell in pure argon atmosphere at different scanning rates, using as a reference an aluminum sample of approximately the same weight of the sample under study (about 50 mg).
Vickers microhardness measurements were made with a load of 3 N on the same sample used for calorimetric scans. The reported hardness values represent the average of at least 5 measurements.

*Table 1: chemical composition (wt%)*

| | Y | RE (Nd) | Zr | Zn | Ag | Mg | Al |
|---|---|---|---|---|---|---|---|
| 7020 | | | | 4.8 | | 1.3 | balance |
| WE43 | 4.2 | 3.3 | 0.6 | | | balance | |
| QE22 | | 2.2 | 0.6 | | 2.1 | balance | |

*Table 2: standard thermal treatments of solutioning and artificial ageing*

| | Solutioning | Ageing T6 |
|---|---|---|
| 7020 | 12h a 480 °C | 12h a 150 °C |
| WE43 | 8h a 525 °C | 16h a 250 °C |
| QE22 | 6h a 530 °C | 10h a 204 °C |

## RESULTS

A series of calorimetric scans was preliminarily made at different scanning rates in order to explore the amount of emission or absorption of energy (exo/endothermic signals) due to structural transformations. In this way it was possible to select the best scanning rate for the successive analyses, a useful compromise between the need to obtain well defined signals and not to lose any information due to thermal drag phenomena. Figure 1 reports such thermograms for the QE22 alloy as an example. An exothermic signal is consequent to solute atoms aggregation (precipitation), while an endothermic signal corresponds to dissolution or reversion of precipitates initially present before the scanning or formed in the course of scanning. The temperature displacement of the signals as a function of scanning rate confirms that the phase transformations are thermally activated phenomena, for which it is possible to obtain the activation energy. This gives useful indications on the kinetics of processes involved.
A typical outcome of the calorimetric analysis is the identification of the melting point of an alloy or the detection of the formation of undesired eutectics. This analysis is particularly useful for commercial alloys in which the impurities may affect the melting temperature. In Fig.2 some scans up to the melting temperature are reported for the WE43 alloy. The chosen temperature for the solutioning treatment (525 °C), obviously lower than the melting temperature, turns out to be also lower than that of the signal P which can be associated to the dissolution

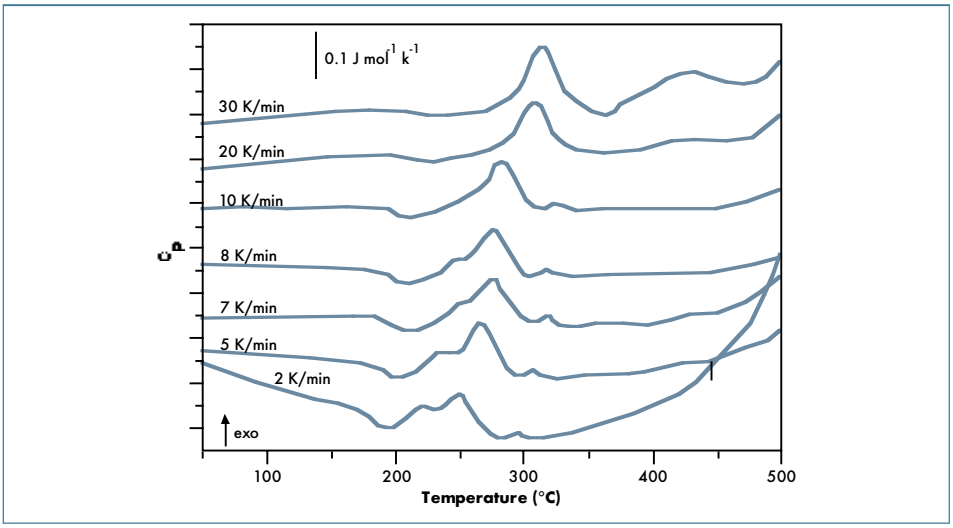


Fig. 1: DSC traces at different scanning rates on the QE22 alloy solutioned and quenched in water. The specific heat at constant pressure obtained by dividing the calorimetric signal (in W/g) by the scanning rate (in K/s) is reported as a function of temperature.

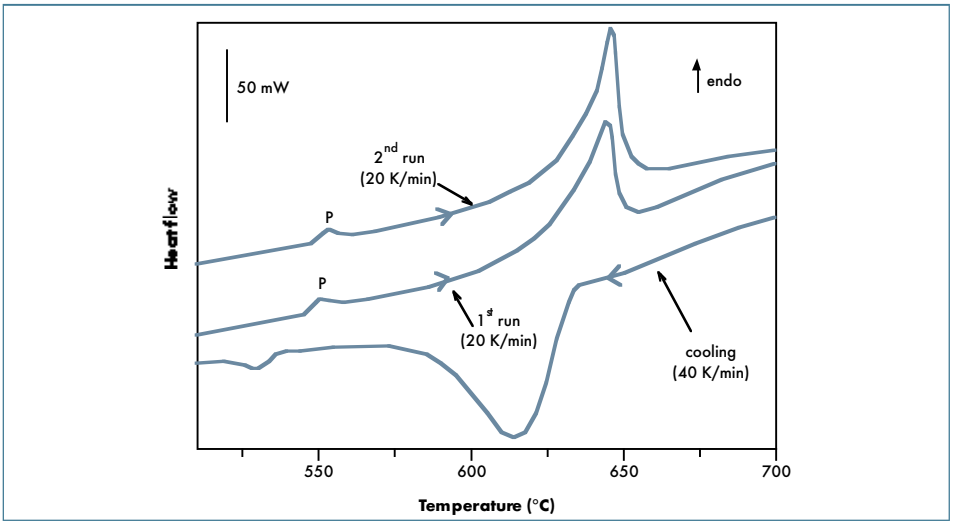


Fig. 2: DSC traces for the alloy WE43 up to the melting temperature.

of a stable phase. The DSC suggests in this case that the solutioning temperature used industrially is too low. Indeed it has been shown [6] that higher solutioning temperatures for this alloy lead to a more homogeneous solid solution, and then to the possibility of obtaining higher increases of mechanical properties following thermal treatments.

The DSC, supported by microhardness measurements, reveals a high potentiality in following the microstructure evolution due to thermal treatments and in correlating it to the evolution of mechanical properties. In Fig.3a the calorimetric traces for samples of quenched 7020 alloy aged at room temperature for increasing times are shown. The endothermic signal D which can be associated with the dissolution of atomic aggregates (Guinier-Preston zones, GPz) formed on ageing at room temperature is clearly observable. The longer the ageing time, the more extended is the D signal and consequently the amount of GP formed in the course of ageing is also higher. The hardening effect of these precipitates is well evidenced by the curve in Fig.3b showing a very good correlation between the hardness increase and the increment of the D signal.

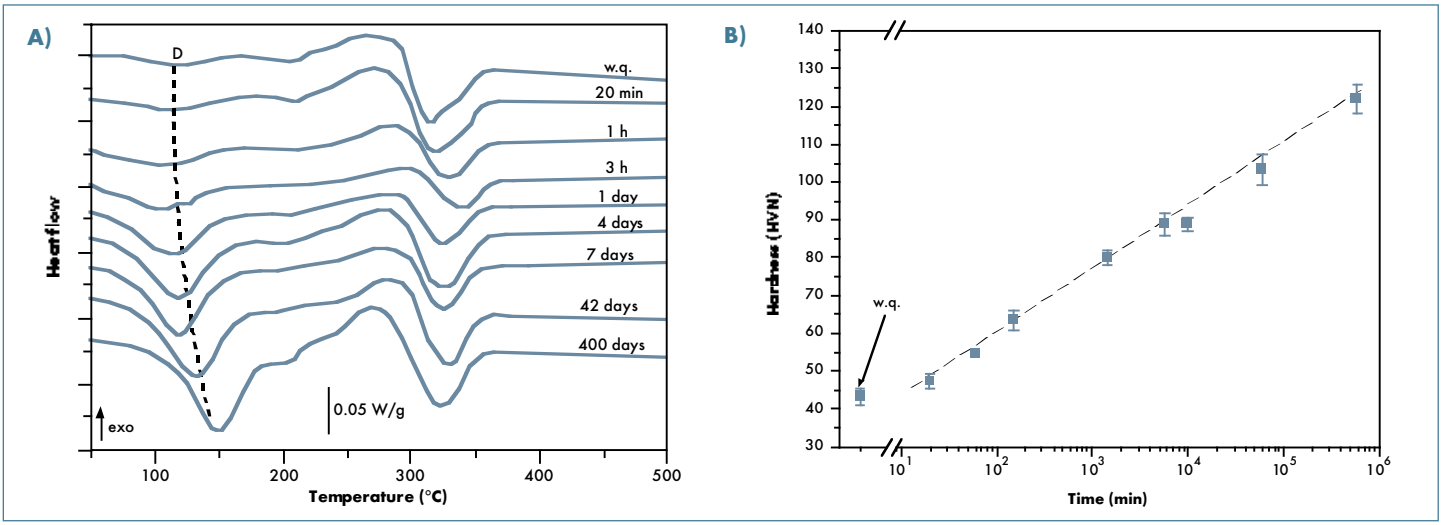


Fig. 3: a) DSC traces for the 7020 alloy aged at room temperature for the labeled times and b) corresponding hardness values.

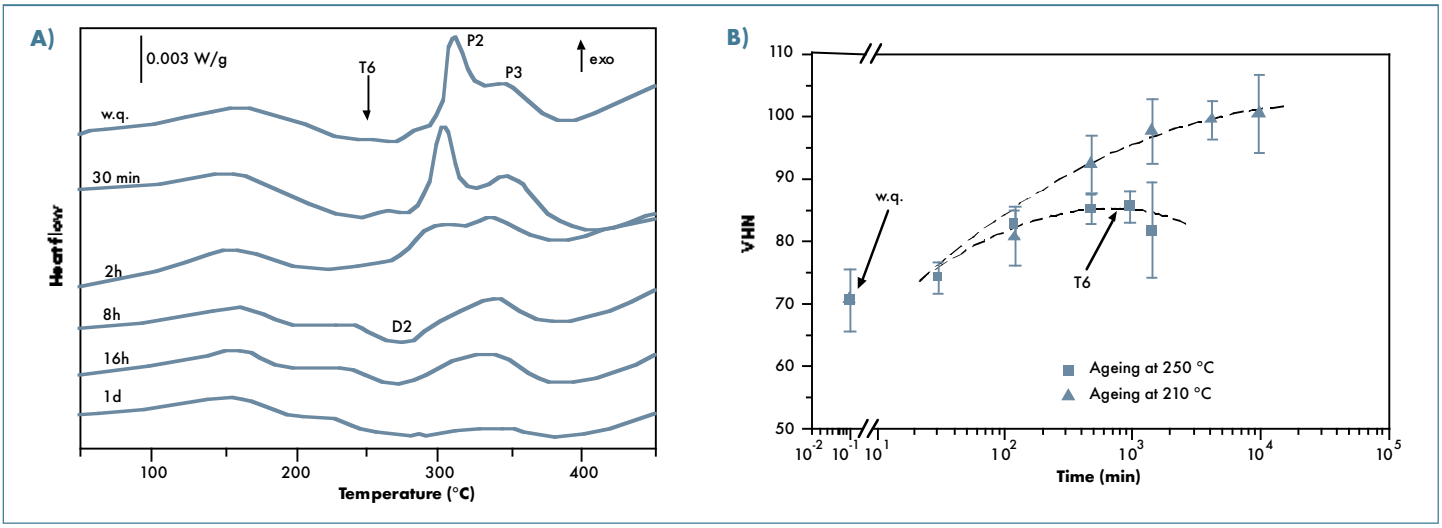


Fig. 4: a) DSC traces for the WE43 alloy aged at 250 °C for the labeled times and b) corresponding hardness values compared with the trend at 210 °C.

In an analogous manner, by the DSC analysis of the type of the forming phases and their contribution to mechanical properties it is possible to optimize the thermal treatments taking advantage of direct observations by TEM [6, 7, 9, 11, 14].

In Fig.4a the evolution of the WE43 alloy is shown at the industrially adopted peak ageing temperature T6 (250 °C).

The above thermograms indicate that the temperature value of 250 °C, considering also the shift due to the scanning rate, is positioned approximately in a range in which an endothermic signal of dissolution occurs in the as-quenched sample. Therefore the temperature of 250 °C would not be suitable for creating metastable hardening phases that would dissolved at this temperature. Furthermore, as the ageing proceeds, P2 and P3 exothermic signals progressively disappear, thus indicating that during the previous thermal treatment stable phases, detrimental to mechanical properties, are formed. The microhardness trend (Fig.4b) confirms the effect of the formation of such undesired phases: the gain in hardness comes to an end after annealing times shorter than the one used for the T6 treatment (16h at 250 °C). On the contrary, it has been shown [7] that a conveniently lower temperature of 210 °C, suggested by DSC measurements, allows to form only the desired metastable phases and then to produce a higher hardness increase in times conveniently shorter than those commonly used in the commercial T6 treatment (see Fig.4b).

Through calorimetric analysis it is possible, on the one hand, to evidence the mechanisms underlying multistage thermal treatments, and on the other, to take

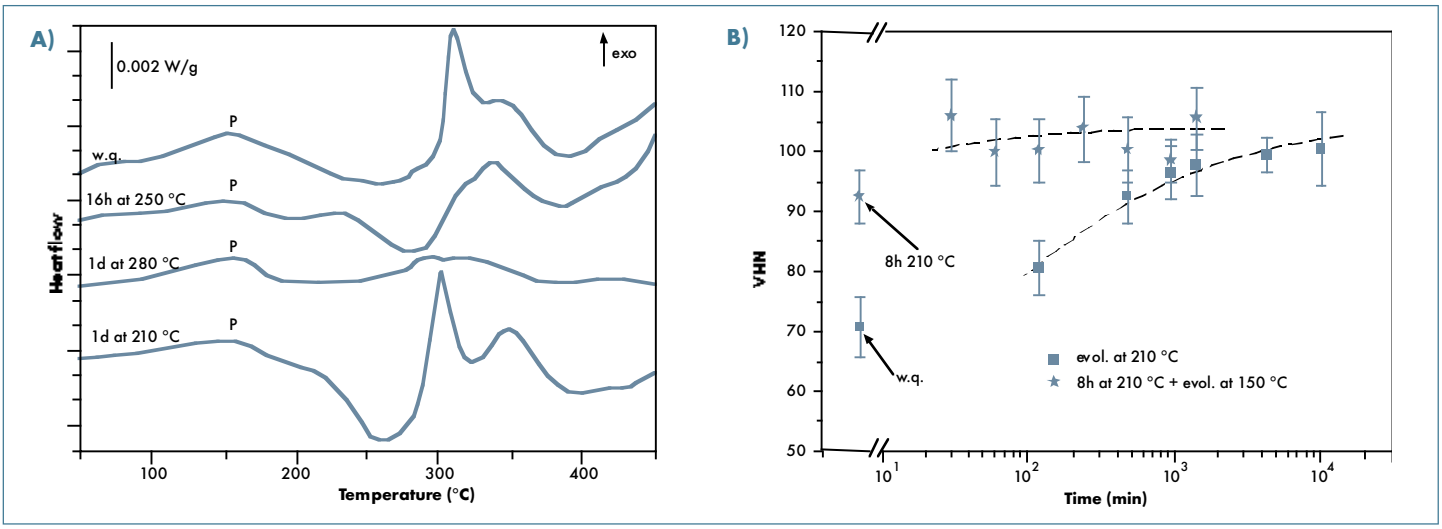


Fig. 5: a) DSC traces for the WE43 alloy aged at the labeled temperatures and times, and b) comparison between the hardness values for an annealing at 210 °C and for a double-stage treatment.

advantage of these phenomena to design suitable thermal treatments. An example of this is the WE43 alloy. In Fig. 5a calorimetric traces are reported after lengthy treatments at relatively high temperatures.
The persistence of the exothermic signal P centered at around 150 °C can be observed, indicating that during scanning a further precipitation of metastable phases occurs; that is, a secondary precipitation takes place. To make the best use possible of this phenomenon a suitable double-stage treatment [8] was designed in order to further increase the hardness of the previously aged material. Indeed, a higher hardness increase was achieved with respect to the one obtained using a classic T6 treatment and with respect to an optimised single stage treatment (Fig.5b). Moreover there was a noticeable energy saving due to reduced times and temperatures.

## CONCLUSIONS

The calorimetric scan is confirmed to be a sort of dynamic tool enabling to characterize the initial structure of an alloy, as well as to follow its evolution as a function of (time and) temperature on the basis of thermal effects associated to phase transformation induced by heating.
The reported examples show how DSC is a very helpful tool for the analysis of phase transformations in thermodynamically metastable materials such as the precipitation hardenable light alloys considered here.

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