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THE USE OF DSC IN DESCRIBING THE STRUCTURE EVOLUTION OF AN AlZnMg ALLOY

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The potential of DSC in suggesting modifications of thermal treatments of Al alloys to increase mechanical properties is described. Significant results can be obtained from calorimetric evolution after a series of annealings, even without a direct observation of the microstructure. The role of a reference baseline is discussed. The Guinier–Preston (GP) zones formation, dissolution or transformation is followed, and their relevance for the microhardness increase is shown, for an AlZnMg alloy of technical interest. Multi-stage thermal treatments have been confirmed to be beneficial. A secondary precipitation occurs at room temperature after annealing at temperatures at which primary precipitation is almost complete.

Keywords: *aluminium alloys, DSC, microhardness, phase transformations*

Introduction

A detailed knowledge of the metastable structures transformation, obtained by quenching an Al supersaturated solid solution, and their thermal stability during heating has become of primary importance to forecast suitable procedures that may improve mechanical and/or chemical properties. A renewed interest for precipitation hardening studies of commonly used compositions has recently emerged [1, 2] when thermal cycles prior to the classic artificial ageing at high temperatures have been adopted. In particular, a short annealing at high temperature followed by a more or less long anneal at room temperature (or slightly higher) has been proved to significantly increase the mechanical properties. A more detailed investigation on the very early stages of the lattice reorganisation of a metastable solid solution has been necessary. Several, and in some cases new, investigation methods have been used to clarify the fundamental role of lattice defects that, introduced in the preparation routes, successively condition the solute atoms mobility. Besides the classic TEM/HRTEM observations and the mechanical tests, Atom Probe Field Ion Microscopy (APFIM) [3], Nuclear Magnetic Resonance (NMR) [4], and Positron Annihilation Spectroscopy (PAS) [5] have given a significant improvement to the study of the earliest nanoprecipitates. The calorimetric measurements have also given useful information on the overall structure evolution on heating, but their use has not been so extensive, probably due to the difficulty in obtaining unambiguous and reproducible results on the heat amount and sign during the thermal scans.

Aim of this paper is to show that differential scanning calorimetry (DSC) has a primary importance in suggesting modifications to the thermal treatments of materials used in the industrial practice. The heat evolution during a temperature scan is a sort of fingerprint of the starting conditions: in other words, if an energetic phenomenon (like a phase transformation, a precipitation or a dissolution) takes place during a controlled heating, one can reasonably suppose that the corresponding structural state was not present prior to the scan. Clearly, the exact knowledge of composition and thermal history of the material is fundamentally important to make some hypothesis on its structure transformation even without a direct observation.

Understanding the thermal evolution of a structure is a necessary condition for designing modifications able to give a certain final structure with particular properties. In this paper this is done, by reporting DSC and microhardness evolution of an AlZnMg alloy submitted to different thermal treatments. In a previous paper [6] we have shown that a multi-stage treatment could give satisfactory results, and a comparison has been made with the secondary ageing effects above reported. Here we perform a new series of treatments to validate and extend the considerations made, using basically DSC results.

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Experimental

Materials and methods

Disc shaped samples have been punched from slices about 1 mm thick of a high purity Al–4.8Zn–1.3Mg (mass%) alloy. The samples have been homogenized, solutioned at 465°C for 1 h and quenched in water at room temperature. Thermal treatments have been performed in an air-circulating furnace with a stability of ±1°C. Details on experimental conditions are given in [6]. A DSC-TA 2010 instrument has been used, in which samples of about 50 mg in mass and pure Al as reference are heated at a scanning rate of 20 K min^{-1} in a protective Ar atmosphere. Here we have to emphasize the unnecessity of a reference baseline. The signals evolution after each thermal treatment is in fact sufficiently clear to assign an exothermic or an endothermic effect, even if in the majority of the cases a quantitative evaluation of the energy involved is not possible. Few examples are known [7, 8] in which enthalpic measurements of precipitation reactions have been made by DSC, in Cu-based alloys.

The attribution of small apparent deviations from the linearity of the differential signal can be unambiguously made when some conditions are fulfilled. The recent paper of Starink [9], for example, clearly deals with the precautions that should be adopted for the interpretation of a DSC trace, including sample preparation. Of course, an approximate knowledge of the possible transformations that a given composition can pass through is a good guideline for assigning an endothermic or exothermic manifestation to a particular structure modification, as we will show in the following. On the other hand, the controversial question on how to measure or calculate a baseline for systems undergoing complex structural modifications on heating is not important here. In addition, the subtraction of a baseline obtained by canonical methods, i.e. at empty cell or with sample and reference in the same conditions, is often misleading when the detected signals are small. Small perturbations, in fact, due to a not perfect reproducibility of the trace may generate spurious and not significant signals which may overlap with signals due to real structural transformations. The assignment of a deviation from the baseline linearity to a calorimetric signal is reasonable, and becomes unquestionable, if it evolves regularly (in amplitude or in temperature) as a consequence of a structure modification after thermal treatments. Moreover, the apparently speculative character of some assignments without a direct observation does not alter the fact that DSC is a primary tool to collect informations on the initial state of a structure and on its evolution, as we will show in the following.

If used in connection with microhardness measurements, as in our case, the DSC gives a powerful hint to optimise the preparation method of a material. We have used a Vickers indenter with a load of 200 N, on the same samples successively submitted to the calorimetric scans.

Results and discussion

In a previous paper [6] we have shown that a multistage treatment of 4 days at room temperature after quenching, followed by an annealing at 95°C for about 200 h gives as a result the highest hardness increase. This was ascribed to the stabilization of the Guinier–Preston zones (GPI) formed immediately after quenching and grown at room temperature, and their progressive transformation into GP(II), an intermediate structure between the zones and the main precipitate η-(Zn_2Mg). It was shown that: 1) the formation during a pre-heating of the equilibrium η phase (revealed by the progressive disappearance of its calorimetric signal during a successive scan) limits the microhardness increase, and 2) also an interrupted ageing at 150°C followed by a natural ageing at room temperature does not increase appreciably the hardness. Here we have extended the thermal cycles to more complex treatments with the aim to find a general route for optimising a fundamental property of the material, like the hardness. This can be done without loosing the practical applicability of the adopted methods to real industrial cases, for which temperature and time are parameters of primary economical importance.

In Fig. 1, the DSC traces (panel a) are shown for samples aged 30 min at 150°C immediately after quenching, then maintained at room temperature for 1 day before a final heating at 95°C for increasing times up to 7 days. In the same figure, the microhardness trend (panel b) is reported for the same samples. Initially, an endothermic signal appears (D1 in the curve at zero time), due to the dissolution of small aggregates or GPI zones newly formed during ageing at room temperature. The short heating at 150°C has mainly the effect of dissolving the zones formed immediately after quenching, having the result of slowing down the hardness increase. Little can be said on the other energetic manifestations prior to the exothermic peak P, due to the precipitation of the η phase, and the final endothermic dissolution.

At increasing dwell times at 95°C (a temperature near the solubility limit of the GP zones [10]), the signal D1 shifts towards higher temperatures. In the meantime, a small bump D2 begins to appear around 200°C and it grows in amplitude with the annealing time. Taking into account the higher diffusivity of Mg with respect to Zn, this is most probably due to a partial transformation of the GPI zones, formed immediately after quenching, into its variant GPII containing

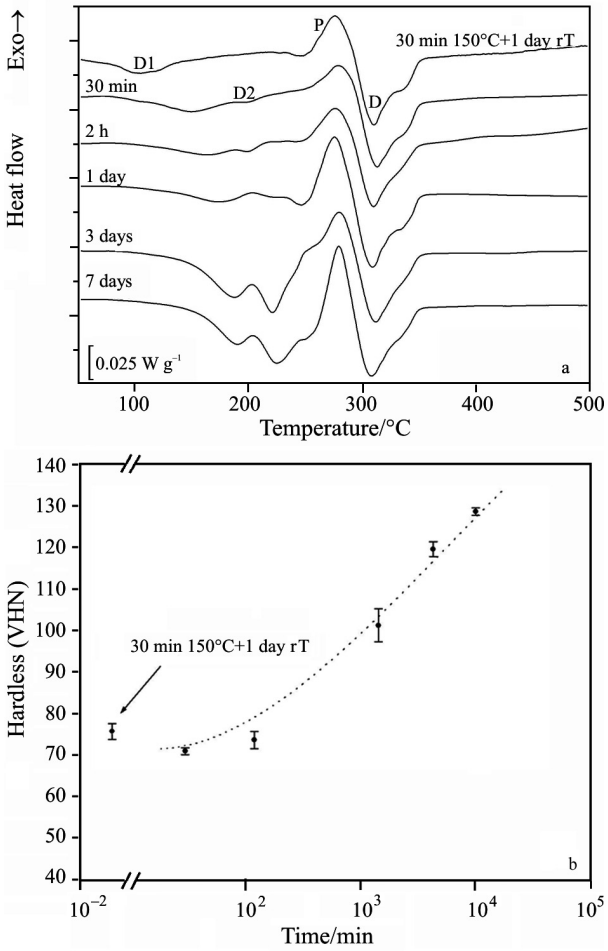

Fig. 1 a – DSC traces on samples quenched, heated for 30 min at 150°C, 1 day at room temperature and at 95°C for the labelled times. Scanning rate: 20 K min^{-1}. b – Vickers microhardness as a function of the annealing time at 95°C (the dotted line is an eye guideline)

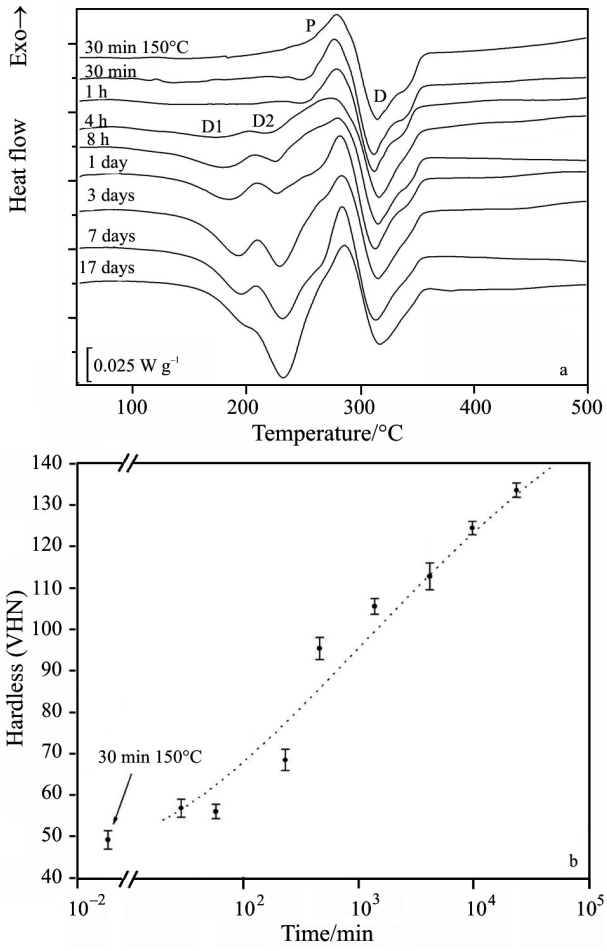

Fig. 2 a – DSC traces on samples quenched, heated for 30 min at 150°C and at 95°C for the labelled times. Scanning rate: 20 K min^{-1}. b – Vickers microhardness as a function of the annealing time at 95°C (the dotted line is an eye guideline)

a higher amount of Mg. The signal *P* remains unchanged, indicating no precipitation prior to the calorimetric scan. The microhardness trend supports these considerations: a progressive increase due to zones formation (revealed by the dissolution signals D1 and D2) is shown up to about 130 VHN. The peak hardness value is not reached even at the highest annealing time of 7 days: the decreasing effect of the main precipitation doesn't yet occur, as shown by the persistence of the precipitation peak *P*.

Similar considerations can be made from the results reported in Fig. 2 (panel a), in which the evolution at 95°C is followed after a pre-heating at 150°C for 30 min (always after quenching). After some hours of heating, a new zone formation is visible, as shown by their dissolution in DSC traces at around 200°C. The hardness (panel b) starts from lower values, due to the reduced contribution of the zone now dissolved, and it reaches values not dissimilar from the preceding ones.

Heating again the samples at 150°C, after a preheating at the same temperature and a dwell time of 8 h at 95°C, has the effect (Fig. 3, panel b) to increase initially the hardness at about 100 VHN, but not to modify substantially its final value. This is due to the formation of η, as evidenced by the progressive disappearance of the signal *P* after 3 h of annealing at 150°C (Fig. 3, panel a).

A further confirmation of a secondary precipitation occurring at room temperature after a primary transformation at 150°C is given by the results in Fig. 4. Here the samples have been pre-aged at 150°C for 2 days, that is at temperature and times at which primary precipitation is almost complete.

We can observe only a large dissolution (panel a), without any appearance of exothermic effects during the scanning. As a consequence, the hardness (panel b) starts from a relatively high value of about 80 VHN, due to an initial solute aggregation at 150°C, and finally it grows slowly. It is interesting to note that age-

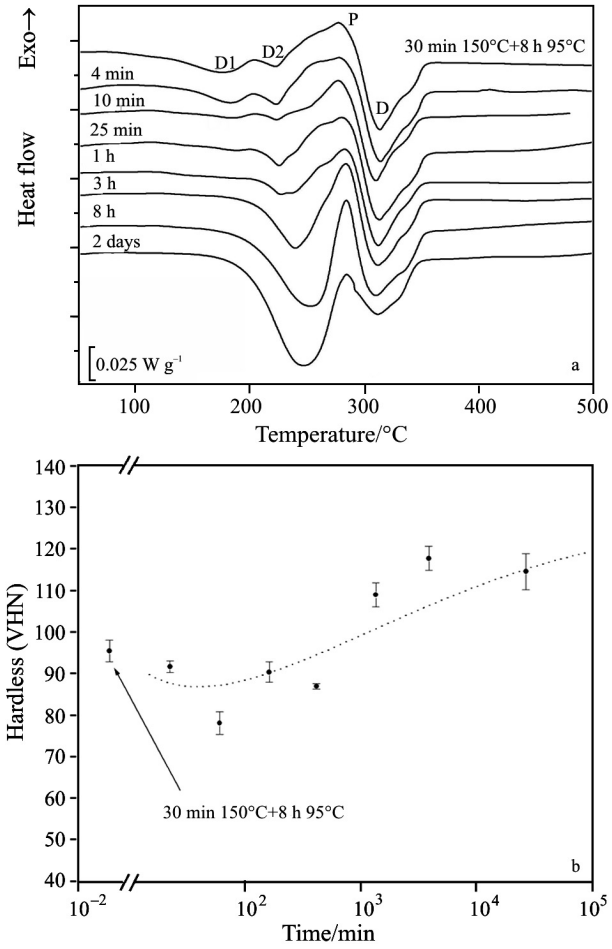

Fig. 3 a – DSC traces on samples quenched, heated for 30 min at 150°C, 8 h at 95°C and at 150°C for the labelled times. Scanning rate: 20 K min^{-1}. b – Vickers microhardness as a function of the ultimate annealing time at 150°C (the dotted line is an eye guideline)

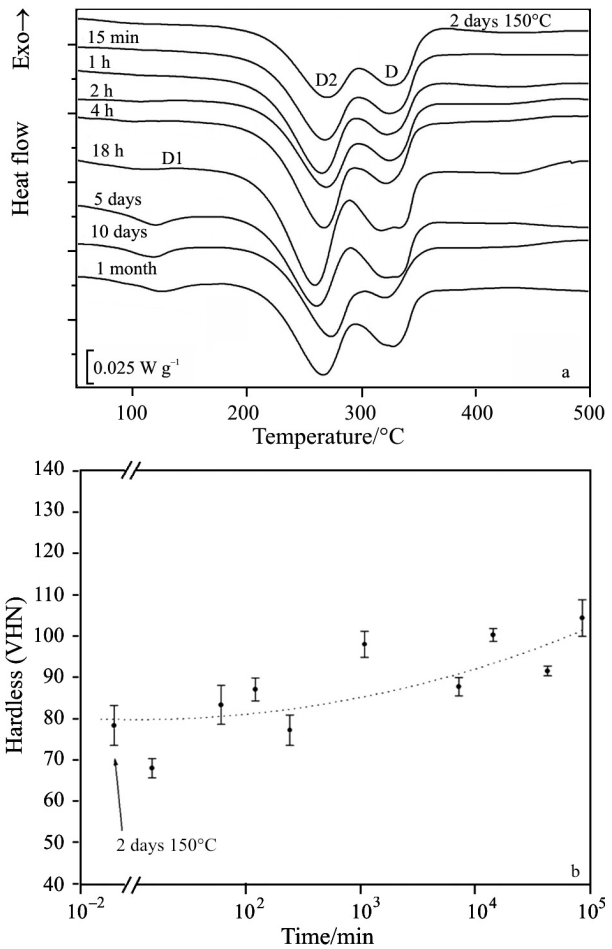

Fig. 4 a – DSC traces on samples quenched, heated for 2 days at 150°C and at room temperature for the labelled times. Scanning rate: 20 K min^{-1}. b – Vickers microhardness as a function of the annealing time at room temperature (the dotted line is an eye guideline)

ing at room temperature for some hours gives origin to a new precipitation, revealed by the presence of an endothermic signal around 100°C (more evident after 18 h). A new aggregation of solute atoms occurs from a solid solution whose saturation degree is now less than the one obtained immediately after quenching. This justifies the small hardness increase at long ageing times. To our best knowledge, this is the first evidence by DSC of a secondary precipitation from a matrix rich in a stable phase, even if a more direct observation could be necessary.

Conclusions

- DSC is an essential tool to give information on the structure evolution in materials submitted to thermal treatments. The signals evolution gives a fingerprint of the starting condition which in most cases may suggest modifications of the preparation route with the aim to increase the mechanical properties.
- For the AlZnMg alloy of this study, an annealing at 95°C, following or not an ageing at room temperature, has been confirmed to be the best way for stabilizing a GP zones structure, which is responsible for the microhardness increase.
- A secondary precipitation is observed at room temperature in samples in which primary precipitation has been nearly completed.

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