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INTERPRETATION OF DTA CURVES FOR MICROSTRUCTURE CHARACTERIZATION OF A COMMERCIAL Al–Zn–Mg ALLOY (7015), AIDED BY CONDUCTIVITY AND HARDNESS MEASUREMENTS

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Hardness and conductivity measurements are shown to be useful to help the interpretation of differential thermal analysis (DTA) curves for aluminium alloys in different metallurgical states. In particular, a commercial Al–Zn–Mg alloy (7015) is studied in four metallurgical conditions. The results of the present analysis are compared with recent studies carried out by other authors on similar alloys by means of transmission electron microscopy (TEM) and differential scanning calorimetry (DSC).

Thermal analysis techniques are rapidly becoming a valuable tool in identifying solid state reactions in aluminium alloys [1–10]. To gain confidence in these techniques as the main method to characterize the matrix precipitate of an alloy in a particular metallurgical state the data obtained from thermal analysis (DTA or DSC) have to be correlated with those obtained by other well established techniques such as TEM among others. This has been done in recent years on a variety of alloys and tempers [6, 8–10]. These studies will hopefully build up a solid basis for the use of DTA and DSC in the rapid identification of the matrix microstructure of aluminium alloys [6]. A further advantage of thermal analysis is the possibility of studying quantitatively the kinetics of solid state reactions in alloys [6, 10].

It is the purpose of this paper to present a study of the microstructure of a commercial Al–Zn–Mg alloy (7015) in different metallurgical states, by means of DTA, hardness and conductivity measurements. The matrix microstructure of Al–Zn–Mg alloys in different metallurgical states are being currently studied [1, 2, 6–14] and, although some points are still controversial, the main questions concerning precipitation processes in these alloys have already been clarified. Although depending on different factors a large number of metastable phases have been identified [7, 11], it is nowadays widely accepted that precipitation in the 7000 series (Al–Zn–Mg and Al–Zn–Mg–Cu alloys) takes place in the following simple sequence [2, 12]: supersaturated solid solution $\Rightarrow$ Guinier-Preston (G. P.) zones $\Rightarrow$ coherent or semicoherent η' phase ($MgZn_2$) $\Rightarrow$ incoherent η phase ($MgZn_2$). Recently a metastable phase diagram for this sequence has been inferred from different experimental data [11]. The description of the characteristics of the above mentioned phases can be found elsewhere [14], here suffices it to note that their relative thermal stability is as follows $\eta > \eta' >$ GP zones.

In this work the main emphasis will be placed on the correlation of the data obtained from DTA with those given by the other two measurements. This is

carried out by measuring the change of Vickers hardness (VH) and conductivity (σ) during a linear heating programme similar to that provided by the DTA equipment. Our results indicate that VN and σ measurements are a useful way to facilitate the interpretation of DTA curves for aluminium alloys.

Experimental procedures

The material used in this work had been d.c. casted, homogenized and hot rolled up to a thickness of 7.5 mm. Its composition in weight per cent was the following: 4.92 Zn, 1.85 Mg, 0.20 Fe, 0.14 Si, 0.15 Zr, 0.11 Cr and 0.06 Mn. Samples of two different sizes were prepared: i) $40 \times 70 \times 7$ mm specimen for hardness and conductivity measurements, and ii) discs of 6 mm diameter $\times 1$ mm thickness for DTA.

The alloy was investigated in four different metallurgical conditions, namely: 1) Annealed, that is heat treated at $310 \pm 5°$ for 2 hrs and cooled very slowly down to room temperature, 2) Solubilized condition, which was obtained by heat treating the alloy for 1 hr at $465 \pm 5°$ and then quenched in water at room temperature, 3) Naturally aged; to obtain this condition the solubilized material was kept at $25 \pm 1°$ for 7 days and, finally, 4) Double ageing which was achieved by heat treating the naturally aged material at $130 \pm 1°$ for 5 days. The low temperature heat treatments (below 200°) were performed in either oil or aqueous thermostated baths, whereas for high temperatures an air furnace was used, the temperature control being accurate to $\pm 1°$ and $\pm 5°$ respectively. If linear heating runs could not be made inmediately after heat treatments, the samples were kept, when needed (solution heat treated samples), in liquid nitrogen.

The DTA measurements were performed using a Mettler TA 2000 commercial instrument. To increase the sensitivity of the measurements, high purity aluminium was used as reference. The runs were carried out at a heating rate of 4°/min, from 30° to 450°. All experiments were performed under a dynamic nitrogen atmosphere (5×10^{-5} m^3/min). Conductivity and Vickers hardness were measured at room temperature on specimens previously polished and linearly heated in a sand fluidized furnace at 4°/min, up to different temperatures (an error of $\pm 2°$ was estimated) and then quenched in water at room temperature. The conductivity σ was measured by means of a Sigmatest – T instrument type 2.067 and the load used to measure the Vickers hardness was 1 Kg. The DTA measurements and the linear heating experiments to measure σ and VH were performed at least twice for each condition; good reproducibility was found.

Results and discussion

Annealed condition – The results for this metallurgical state are shown in Fig. 1. In the annealed condition the alloy reaches its maximum conductivity and its minimum strength. This indicates that the solid solution has attained the maximum

degree of decomposition, and that the phase present should be incoherent with the underlying lattice. Consequently, the only precipitate in the annealed state should be the incoherent η phase ($MgZn_2$) [1, 6–9]. Therefore the single endothermic peak in the DTA curve for this condition should represent the dissolution of the η phase [1, 2]. This interpretation, although evident, is backed by the behaviour of σ during the linear heating, as it decreases monotonically down to the value corresponding to the solubilized condition. It may be noticed that the

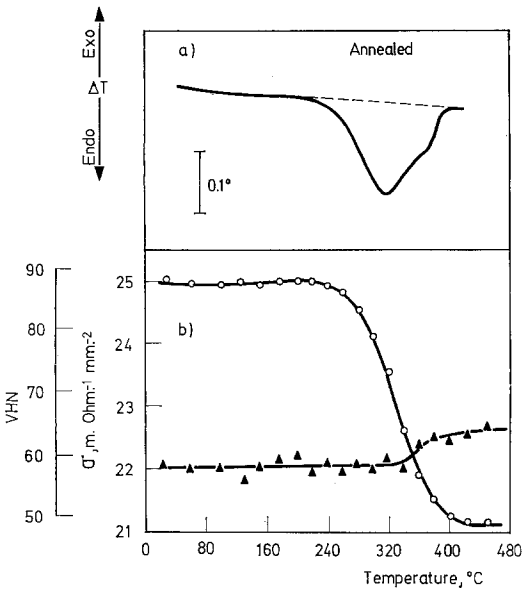

Fig. 1. a) DTA curve (heating rate 4°/min) and b) Change of conductivity (0) and Vickers hardness (▲) during a linear heating at 4°/min., for the annealed Al–Zn–Mg alloy

temperature range along which σ varies, nearly coincides with that of the DTA peak. Moreover the maximum of the endothermic peak occurs at a temperature lying in a region where σ is varying most rapidly; although in this work it has not been possible to check if the temperature of the maximum of the DTA peak exactly coincides with that at which σ varies most rapidly, this result might give support to the assumption made by Kissinger [15] to derive kinetic data from non-isothermal studies, namely, that the maximum of the DTA peak coincides with the maximum rate of reaction. The Vickers hardness also varies in the same temperature range as σ, it increases from the value corresponding to the annealed condition up to that characteristic of the solubilized condition. In this metallurgical state, it is clear that VH is a less useful property than σ, to interpret the DTA peak.

Solubilized condition – Figure 2 shows the DTA, σ and VH results for this condition. In the DTA curve a very weak endothermic reaction below 160° is

first noticed, followed by an exothermic reaction between 160° and 256° peaking at 216° and an endothermic reaction between 256° and 390°. The processes associated with these reactions can be identified by means of the σ and VH results [10]. The weak endothermic peak below 160° is clearly associated with G. P. zones; in fact instead of a single reaction, two should be present, one accounting for the formation of G. P. zones (exothermic) and the other for its dissolution (endothermic). Actually a slight deviation of the base line could give two reactions

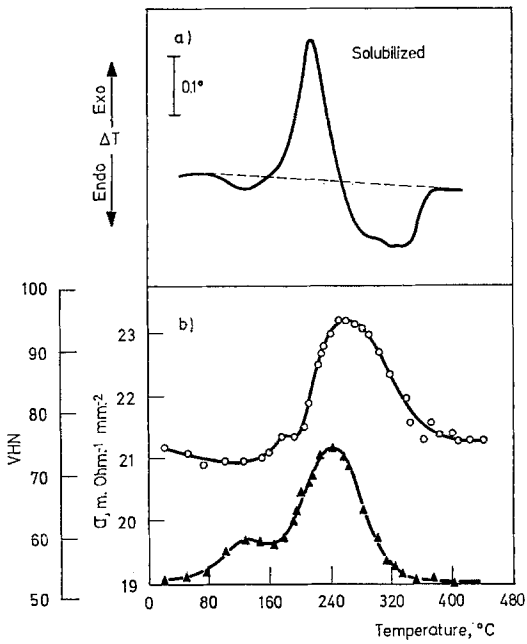

Fig. 2. As Fig. 1 but for the solubilized Al–Zn–Mg alloy

instead of the one shown in Fig. 2. These reactions occur due to the very low heating rate used in this work, in fact if higher heating rates are used no reactions take place below 160° [13]. It should be pointed out that these reactions were not observed by Asano and Hirano [1] in their early studies of Al–Zn–Mg alloys; their results are otherwise in agreement with those reported in this paper (see below and refs. [1, 2]). The σ and VH results support the interpretation of these features (below 160°) as related to G. P. zones. Initially σ decreases and VH increases revealing the formation of G. P. zones; this interpretation is based upon the fact that the formation of G. P. zones is the only precipitation process which lowers σ below the value corresponding to the solubilized condition [14]. At around 125° σ reaches a minimum and VH a maximum. Above 125° the redissolution of G. P. zone takes place leading to an increase of σ and a decrease of VH. The redissolution of G. P. zones seems to overlap with the formation of the

η' phase as VH does not recover its initial value. The exothermic peak between 160° and 256° has to be related with the formation of η' and η phases and the redissolution of the η' phase [6] as suggested by the σ and VH results. In the region of the DTA peak σ increases indicating that precipitation predominates over dissolution. Again the maximum of the DTA peak (at around 216°) lies in a region where σ varies most rapidly. VH reaches a maximum at 240° suggesting that above this temperature the η' phase dissolves and, as σ is still increasing, the

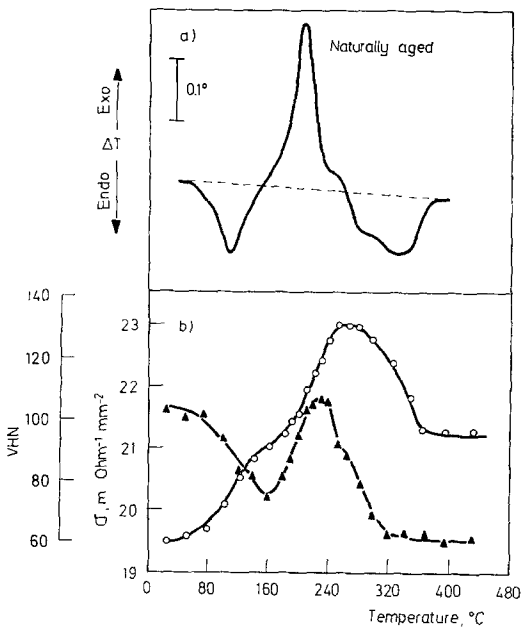

Fig. 3. As Fig. 1 but for the naturally aged Al—Zn—Mg alloy

η phase is being formed. It must be mentioned that in the present work the maximum VH does not coincide with the maximum of the DTA exothermic peak as pointed out inRef. [10]. The beginning of the second endothermic peak (at around 256°) coincides with the maximum σ, indicating that this peak accounts for the redissolution of all phases. By the end of this peak both σ and VH reach their values for the solubilized condition. Finally it should be noticed that some minor differences between the present results and preliminary results reported elsewhere [10] are due to the different DTA apparatus used in the two studies, the one used in this work giving a better base line (this remark also holds for the naturally aged condition).

Naturally aged condition — The results for this condition are shown in Fig. 3. Three reactions are clearly noticed in the DTA curve. The first endothermic peak lies between 40° and 155° its maximum being at 108°. The monotonic decrease

of VH up to the end of the DTA peak suggests that dissolution predominates over other processes [6]. The very low value of σ for this metallurgical state reveals the presence of G. P. zones. During heating, σ increases monotonically beyond the first DTA peak, nonetheless a shoulder at around the end of that peak indicates that a different process takes place above 155°, specifically, G. P. zones dissolution occurs below 155° whereas above it the formation of the η' phase takes place. It should be remarked that the minimum VH at around 158° is still

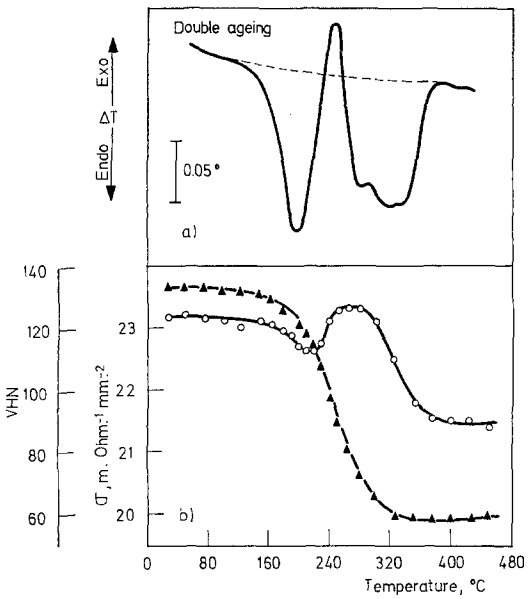

Fig. 4. As Fig. 1 but for the double aged Al—Mg alloy

greater than the value corresponding to the solubilized condition; this might indicate that, as observed by De Iasi and Adler by means of TEM studies [6] the formation of the η' phase is also occurring in the region of the first DTA peak. Nonetheless G. P. zones dissolution should be the predominant reaction [6]. An exothermic peak follows between 155° and 260°, peaking at 185°. As in the solubilized condition, the σ and VH results indicate that formation of η' and η phases and dissolution of the η' phase occur in this region. In this case a shoulder on the exothermic peak (around 240°) is also noticed. In previous work [10] this shoulder followed the base line and was interpreted as particle growth. In fact growth of particles might also be occurring as observed by TEM [6], although it is not necessarily related with the shoulder, which only indicates that several processes are occurring in this region [1, 2]. As in previous cases Kissinger's assumption [15] is supported by the σ and VH results. The third DTA peak (endothermic) lies between 260° and 384° and again accounts for the dissolution of all phases.

Double ageing – Figure 4 shows the results for this metallurgical state. The initial high values of VH and of σ (the latter being lower than in the annealed condition but higher than in the naturally aged and solubilized conditions) indicate that the η' phase is mainly present [6]. During the whole linear heating VH decreases suggesting that the formation of coherent or semicoherent phase (η') does not take place. The DTA curve shows three peaks, the first one being endothermic and lying between 120° and 232°, its maximum being at around 196°. The initial decrease of both σ and VH indicates that dissolution of the η' phase is occurring, nonetheless above 216° σ starts to increase revealing that the formation of the η phase is superimposed on the dissolution of the η' phase. In this case the formation of the η phase is so important that it leads to a weak exothermic peak between 232° and 256°. This peak was not observed by De Isasi and Adler [6] in his study of 7075 alloy in the T7351 temper (similar to the present condition), although their TEM studies showed the formation of the η phase in the region of the first endothermic peak. Minor differences in alloy composition, temper and heating rate may be the cause of this slight discrepancy. The third DTA peak (endothermic) lies between 256° and 404° and accounts for the dissolution of all phases (η' and η). TEM results [6] indicated that this peak is associated only with the dissolution of the η phase. In the present case the dissolution of the η' phase should also occur as VH reaches its minimum value (solubilized condition) at 300° whereas the DTA peak starts at 256°. Nonetheless the dissolution of the η phase is clearly predominant. Again the minimum value of σ is reached at the end of the DTA peak (the alloy is in the solubilized condition).

Conclusions

It has been shown that conductivity and hardness measurements, which provide complementary information on the matrix microstructure which characterizes a particular metallurgical state, are useful in interpreting DTA curves for aluminium alloys. Four extreme metallurgical conditions have been investigated and in all cases the solid state reactions accompanying the DTA peaks have been identified. The results have been compared with those reported by other authors and especially with those obtained by means of TEM studies [6] and the agreement turned out to be rather satisfactory. It is suggested that σ and VH measurements such as those reported here plus TEM studies [6] should be performed in other alloys in order to build up a solid basis for the use of thermal analysis in the characterization of metallurgical states in aluminium alloys.

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ZUSAMMENFASSUNG — Es wurde gezeigt, daß Härte- und Leitfähigkeitsmessungen bei der Interpretation von Kurven der Differentialthermoanalyse von Aluminiumlegierungen in verschiedenen metallurgischen Zuständen nützlich sind. Besonders eine handelsübliche Al–Zn–Mg Legierung (7015) wurde unter vier metallurgischen Bedingungen untersucht. Die Ergebnisse der durchgeführten Analyse wurden mit neueren Untersuchungen anderer Autoren an ähnlichen Legierungen durch Transmissions-Elektronenmikroskopie und DSC verglichen.

Резюме — Показано, что измерения проводимости и твердости могут быть полезными при интерпретации кривых дифференциального термического анализа алюминиевых сплавов различного металлургического состояния. В частности, изучен продажный сплав Al—Zn—Mg (7015) в четырех металлургических состояниях. Результаты проведенного анализа сопоставлениями исследованиями, выполненными другими авторами на подобмых сплавах с помощью электронного микроскопа на ыифференциальной сканирующей калориметрии.