Journal of Thermal Analysis, Vol. 11 (1977) 221–229

THE EFFECTS OF CONCENTRATION AND HEATING OR COOLING RATE ON THE DTA CURVES OF Al–Ce ALLOYS*

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(Received November 30, 1976)

The crystallization of Al–Ce alloys was studied by DTA. The melting and freezing DTA curves of the investigated alloys exhibit two peaks, corresponding to the transformations of a high-purity phase and the eutectic phase, respectively. The peaks could be separated during both freezing and melting by changing the heating or cooling rate. The final temperature of the phase transformation is marked by the starting temperature of the second peak. A slight shoulder on the DTA peak, even on the opposite side to the maximum point, may correspond to the final temperature.

The connection between the reaction time and the peak temperature for the sample was studied at different cooling and heating rates.

It was concluded that a knowledge of the structure and composition of the studied system is necessary in the interpretation of the DTA curves.

The properties of metals are mainly influenced by the crystallization process. The crystallization is determined by the composition of the alloy and the rate of solidification. In other words, it is of great importance how the metal passes through the solid-liquid region.

Technological processes occur far from the equilibrium state, and technical materials contain several alloying elements and impurities. Therefore, the data available in the literature do not cover the technical demands. For practical purpose further investigations are necessary.

In order to determine the conditions of solidification, we have applied thermal analysis. We were mainly interested in the liquidus and solidus temperatures and in the time for which the material stays between these temperatures.

In order to start with the simplest system, aluminium of high purity and Al–Ce alloys were studied. Ce, as alloying element, is suitable for thermal cycling, since its melting temperature is much higher than that of aluminium. That is, the Ce concentration remains constant during the melting and freezing cycles. Furthermore, the application of rare-earth metals as addition elements is an up-to-date problem. It is already known that the eutectic concentration is at 10% Ce; the liquidus temperature changes by 10° up to that concentration. A solid solution forms only at very low concentrations (lower than 0.05% Ce), and is not detectable by thermal analysis.

* Paper presented at the Scientific Session on Thermal Analysis held at Balatonfüred, Hungary, on 14–16 October, 1976.

Experimental

The effects of Ce concentrations between 0 and 13% and of heating and cooling rates between 1.5 and 0.2°/min were studied. Differential thermal analysis was carried out in an air atmosphere, using a Mettler thermal analyser. A platinum-rhodium thermocouple (DTA 21) and an Al_2O_3 microcrucible were applied. The mass of the sample was approximately 100 mg. Samples were taken from an as-cast bar and turned to a shape identical with that of the microcrucible.

In interpreting the thermal curves, we faced the problem of the correct determination of the starting and final temperatures of the phase transformation. It was recently reported by Willmann [1] that the temperature determined in accordance with the ICTA proposal (extrapolated onset, T_{on}) differs from the true value, i.e. from the temperature determined by the point where the DTA curve departs from the base line for the first time (departure, T_{dep}).

Results

The melting and freezing DTA curves of the investigated alloys exhibit two peaks (Fig. 1).

Metallurgists have already established that the last step in the solidification of metals is the solidification of eutectic melt enclosed by the growing solid phase. Assuming that the second peak corresponds to the solidification of this eutectic phase (which may be characterized by isothermal phase transformation), we performed stepwise cooling (Fig. 2).

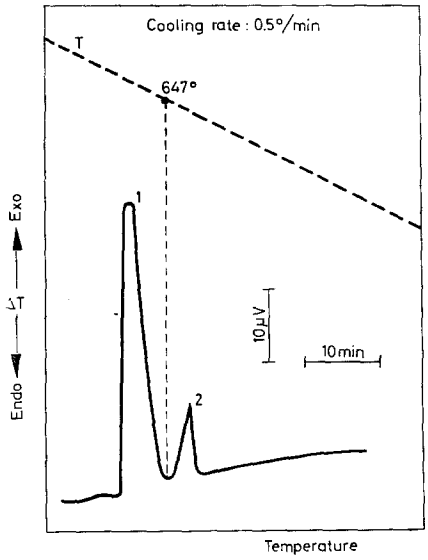

Fig. 1. Characteristic DTA curve for the investigated alloy

It can be seen that if the solidification is stopped, the remaining melt does not solidify as long as a particular temperature has not been reached. When the cooling is stopped at this certain temperature, the solidification is accomplished even under isothermal conditions.

We conclude that in the investigated alloy the final temperature of the phase transformation is marked by the starting temperature of the second peak.

In order to determine the starting temperature of the transformation, both freezing and melting DTA curves were evaluated. Supercooling was taken into consideration.

The effect of Ce concentration was studied first by metallography (Fig. 3). It is easy to recognize that two solidifying phases are present. The ratio of the phases corresponds to the change of Ce concentration. The increase of the eutectic phase and decrease of the pure aluminium at the same time can be seen.

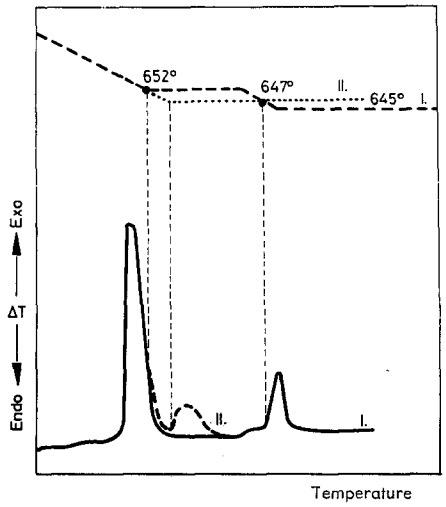

Fig. 2. The stepwise cooling proved that the end-temperature of solidification is determined by the start of the second peak

The effect of Ce concentration of the DTA run is shown in Fig. 4. We should like to demonstrate that independently of the concentration, the solidification of the eutectic starts at the same sample temperature. This is the final temperature of the phase transformation.

Interestingly, we have to conclude that depending on the concentration of the addition element, a slight shoulder on the DTA peak, even on the opposite side to the maximum point, may correspond to the final temperature of the transformation.

The characteristic liquidus and solidus temperatures for the different concentrations are shown in the phase diagram of this very simple system (Fig. 5). It should be emphasized that the diagram represents temperatures obtained at a cooling rate of 1°/min. Further investigations on rate effects, however, showed that temperatures were rate-dependent.

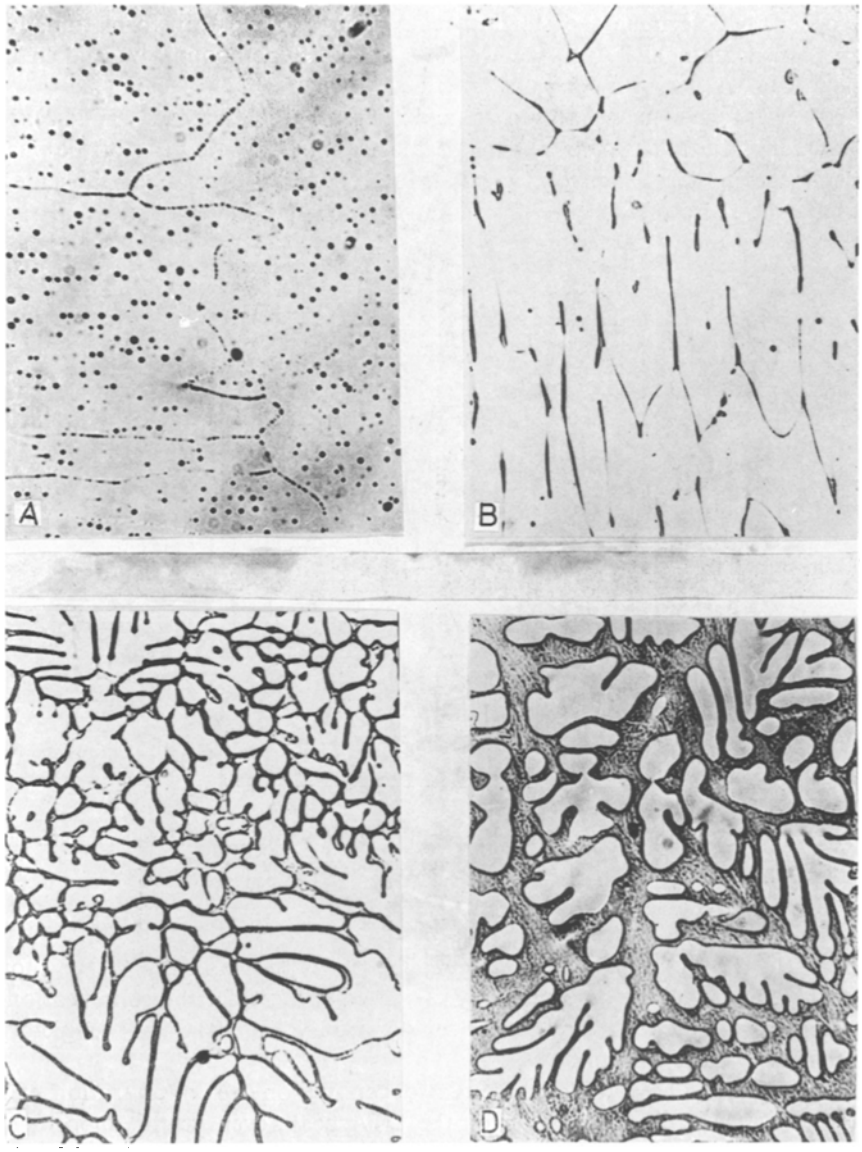

Fig. 3. The effect of Ce concentration on the structure of the alloy. A: 0.26%; B: 0.51%; C: 3.14%; D: 8.25% Ce. Magnification: ×160

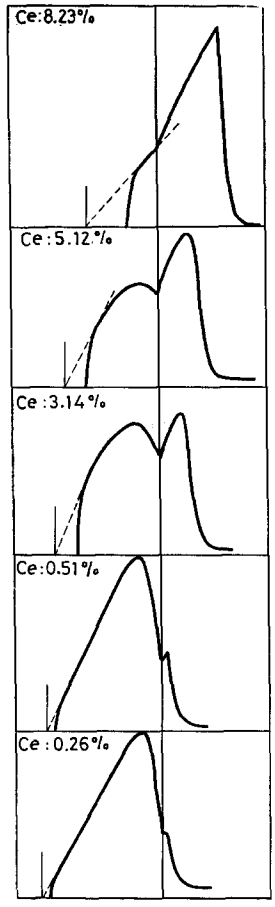

Fig. 4. The effect of Ce concentration on the DTA run. Cooling rate: 1°/min

Various rates of heating and cooling were employed with characteristic concentraitons: pure aluminium (99.999%), the eutectic compound, and the Al–Ce alloy containing 1.71% Ce. This latter is typical as regards the two-peak region.

With aluminium of high purity we could expect that the liquidus temperature is equal to the solidus temperature, i.e. the transformation occurs isothermally. When either the melting or freezing process was taken, a temperature interval was found. The two-phase liquid region decreased with decreasing rate of heating or cooling. The appearance of the solid-liquid interval is not characteristic for the metal itself, but is the consequence of the non-equilibrium conditions. This observation supplements the finding of Wiedemann [2].

Similarly to the case of pure aluminium, the eutectic alloy too shows the solid liquid interval. The extrapolated onset temperature (taken from the DTA curve

of freezing) correlates to the previously determined eutectic temperature and is independent of the cooling rate (Fig. 6).

Further, we investigated the connection between the reaction time and the peak temperature of the sample at different cooling and heating rates (Fig. 7). The

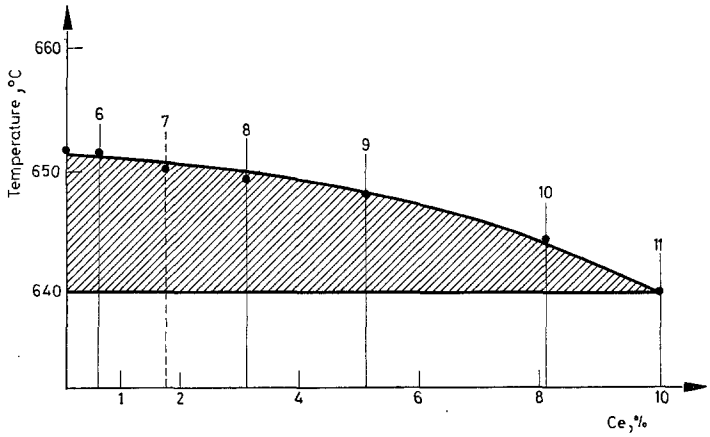

Fig. 5. Part of the phase diagram of the Al—Ce system, determined at a cooling rate of 1°/min. The sample weight was approximately 100 mg. Solid solution was not detected

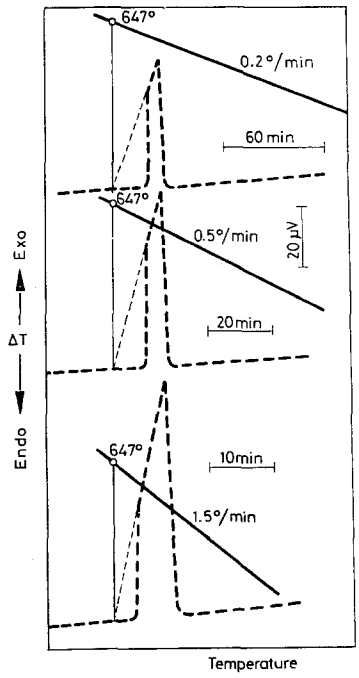

Fig. 6. DTA curves of freezing for the eutectic composition

Figure comprehensively illustrates the phenomena for both high-purity aluminium and the eutectic, on freezing and melting.

On melting, both metals show the same behaviour within an error of about one degree. The sample temperature is determined by the superposition of the heat of fusion and the heating program, assuming that the conductivity of the system

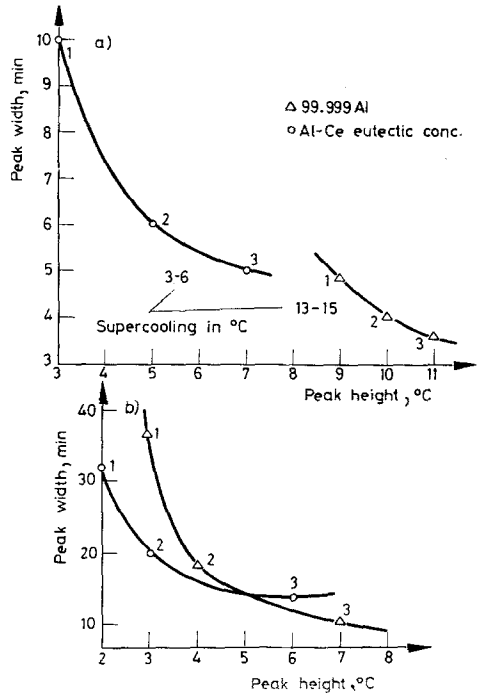

Fig. 7. Connection between the reaction time and the peak temperature of the sample at different cooling (a) and heating (b) rates. 1: 0.2°/min; 2: 0.5°/min; 3: 1.5°/min

is constant. In contrast, during freezing the behaviours of the two metals differ, in accordance with their different abilities to undergo supercooling.

As a consequence of supercooling, the time of reaction decreases and the same amount of latent heat heats the sample to a higher temperature. If the temperature program is too fast, it may occur that the latent heat warms up the sample above the liquidus temperature.

The alloy containing 1.71 % Ce showed the characteristic DTA curve with two peaks. It should be emphasized that one of the peaks corresponds to the transformation of a phase of high purity and the other to the eutectic phase.

The DTA peaks could be separated during both freezing and melting by changing the heating or cooling rate (Fig. 8). Analysis of the characteristic temperatures

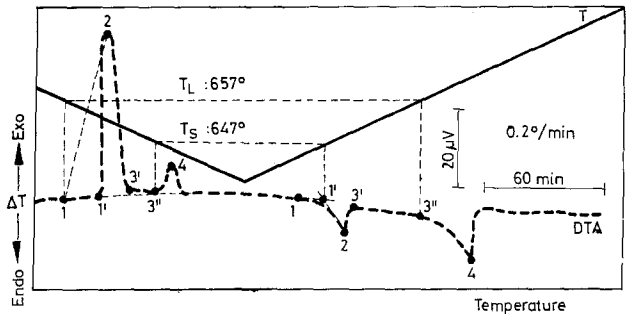

Fig. 8. Characteristics of the DTA curve. The corresponding temperatures are presented in the Table

of DTA run (Table 1) reveals that the T_{dep} of melting (T_1) is independent of the heating rate and is equal to the T_{on} of the second peak ($T_{3''}$) taken from freezing. We regard this temperature as the solidus temperature.

The departure of the second peak in the DTA curve of melting ($T_{3''}$) is also independent of the heating rate. As this peak represents the transformation of the pure phase, the start temperature should be equal to the departure of the DTA curve of freezing (T_1). If supercooling is taken into consideration the measured temperatures agree within an acceptable error. We take this temperature as the liquidus temperature.

The final temperature (T_4) taken from the DTA curve is affected by the temperature program. During melting it decreases and during freezing it increases with decreasing heating or cooling rate. These temperatures are determined by several effects and are independent of the phase transformation.

Table 1

Characteristic temperatures of the DTA run at different heating and cooling rates

°/min	Melting						Freezing					
	1	1'	2	3'	3''	4	1	1'	2	3'	3''	4
1.5	646	648	652	658	657	666	?	658	654	645	—	644
0.5	646	648	650	654	657	665	?	656	658	649	647	646
0.2	647	648	650	652	657	664	?	655	658	650	647	648

Conclusions

In the interpretation of DTA curves several influencing factors should be taken into consideration. Other methods should be used, referring to the composition

and structure of the system investigated. By such combination, thermal analysis can provide further information in metallurgical research.

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The authors are grateful to Mrs. M. Laár for the excellent preparation of the alloys. Thanks are due to Miss K. Papp and Mr. J. Szeleczki for their help in the thermal analysis. We are also indebted to Mrs. M. Horváth for the metallographic work.

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RÉSUMÉ — La cristallisation d'alliages Al—Ce a été étudiée par ATD. Deux pics apparaissent sur les courbes ATD lors de la fusion et de la cristallisation des alliages étudiés. L'un est dû à la transformation de la phase de haute pureté et l'autre à la phase eutectiques. Les pics peuvent être séparés en changeant les vitesses de chauffage et de refroidissement, tant à la fusion qu'à la cristallisation. La température finale de la transformation de phase est marquée par la température initiale du second pic. Un faible épaulement du pic ATD, même du côté opposé au maximum, peut correspondre à la température finale.

Le rapport entre la durée de la réaction et la température du pic a été étudié pour diverses vitesses de refroidissement et de chauffage.

On en conclut que l'interprétation des courbes ATD exige de connaître la structure et la composition du système étudié.

ZUSAMMENFASSUNG — Die Kristallisation von Al—Ce-Legierungen wurde mittels DTA untersucht. Die Schmelz- und Erstarrungs-DTA-Kurven der geprüften Legierungen weisen zwei Peaks auf, welche der Umwandlung einer Phase hohen Reinheitsgrades, bzw. der eutektischen Phase entsprechen. Die Peaks konnten sowohl während des Erstarrens als auch während des Schmelzens durch Änderung der Aufheiz- oder Abkühlgeschwindigkeit getrennt werden. Die Endtemperatur der Phasenumwandlung wird durch die Anfangstemperatur des zweiten Peaks angedeutet. Eine kleine "Schulter" des DTA-Peaks, selbst an der entgegengesetzten Seite des Maximums, kann der Endtemperatur entsprechen.

Der Zusammenhang zwischen der Reaktionszeit und der Peak-Temperatur der Probe wurde bei verschiedenen Aufheiz- und Abkühlgeschwindigkeiten untersucht.

Es wurde gefolgert, daß bei der Deutung von DTA-Kurven die Kenntnis der Struktur und Zusammensetzung des untersuchten Systems nötig ist.

Резюме — С помощью ДТА была изучена кристаллизация сплавов Al—Ce. Кривые ДТА плавления и отвердевания показывают два пика, относящиеся, соответственно, к превращению фазы высокой чистоты и эвтектической фазы. Эти пики могут быть разделены как при плавлении, так и при отвердевании, изменением скорости нагрева и охлаждения. Конечная температура фазового превращения характеризуется начальной температурой второго пика. Небольшое плечо ДТА пика, даже на противоположной стороне точки максимума, может соответствовать конечной температуре. Связь между временем реакции и температурным пиком образца была изучена при различных скоростях нагрева и охлаждения. Сделано заключение, что при интерпретации кривых ДТА, необходимо знание структуры и состава исследуемой системы.