

# Thermal analysis of peritectic alloys

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Predictions that increasing cooling rate will result in increasing elevation of the apparent peritectic arrest temperature have been confirmed for Cd–Ag and Zn–Cu alloys in line with observations of Al–Ti alloys. The shape of the peritectic cooling curve is related to the competition between the peritectic transformation and direct crystallization from the melt in the formation of the secondary  $\alpha$  phase. The effect on solidification of the relative depressions of the  $\alpha$  and  $\beta$  liquidus during cooling is considered.

## 1. Introduction

In thermal analysis of the freezing of single-phase or eutectic alloys it is a general observation that the temperature of any thermal arrest is depressed when the cooling rate of the melt is increased. For peritectic alloys, i.e., for compositions between  $C_{LP}$  and  $C_{\beta p}$  in the formalized diagram of Fig. 1, this observation is reversed. With increasing cooling rate the apparent peritectic arrest temperature increases progressively above the equilibrium peritectic temperature  $T_p$ . This trend was predicted by Boettinger [1] and observed experimentally for Al–Al<sub>3</sub>Ti alloys by Cisse *et al.* [2] and Maxwell and Hellawell [3]. During work on directional solidification of peritectic alloys [4, 5], the opportunity was taken to compare direct cooling curves of several peritectic alloys, as in Figs 2, 3 and 4, in order to test further the trend towards elevation of the arrest temperature. The cooling curves were obtained by placing a thermocouple in an alumina crucible containing approximately 8 cm<sup>3</sup> of alloy. The thermocouple was centrally placed to be distant from the crucible walls and any oxide layer that may form. The alloys were superheated approximately 200° C above the liquidus line and then cooled at a range of rates. Values of  $T_p$  referred to for each of the alloy systems studied were obtained from Hansen [10].

Some anomalies were noted in previous interpretations of peritectic cooling curves and a consistent interpretation is attempted below.

## 2. Thermal sequence

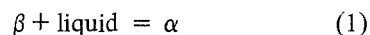
For all alloys tested, the same sequence of cooling

curve features was observed at the slower cooling rates, and this sequence was therefore regarded as “normal” for a peritectic alloy. It can be described with reference to the curves of Fig. 3, which were taken from a Cd–Ag alloy with the composition of the peritectic point, or  $C_{\alpha p}$  in Fig. 1. The sequence is:

- (1) A high temperature arrest on crossing the liquidus line at  $T_L$ ;
- (2) A reduction in slope,  $ab$ , as the peritectic temperature,  $T_p$ , is approached. This is immediately followed by
- (3) An arrest,  $bc$ , at a temperature above  $T_p$  dependent on cooling rate.  $bc$  was never truly horizontal, but sloped down from  $b$  to  $c$ ;
- (4) A sharp change in slope at  $c$  to a uniform cooling rate  $cd$ ;
- (5) A further change in slope at  $d$ , representing the end of solidification.

For Al–Ti alloys (Fig. 2) an additional feature was a long, almost horizontal plateau  $de$  which finished by tailing off rather slowly ( $ef$ ) as solidification was complete. The curves of Fig. 2 are in close agreement with those recorded by Cisse *et al.* [2].

This sequence of slope changes must be related to the freezing sequence. For composition  $C_{\alpha p}$  in Fig. 1 the equilibrium sequence should begin with nucleation of the primary phase below the liquidus and subsequent primary growth. At  $T_p$  the peritectic reaction



should occur and continue until each  $\beta$  particle is

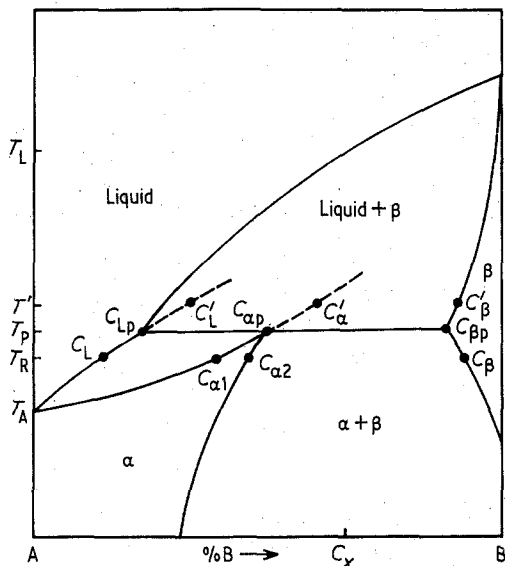
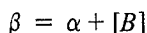
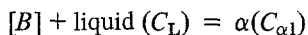


Figure 1 Hypothetical peritectic phase diagram, showing symbols used for phases, compositions and temperatures. Alloys of initial compositions between  $C_{LP}$  and  $C_{\alpha p}$  are hypoperitectic alloys, between  $C_{\alpha p}$  and  $C_{\beta p}$  are hyperperitectic alloys, between  $C_{LP}$  and  $C_{\beta p}$  are peritectic alloys,  $< C_{LP}$  are non-peritectic alloys, where  $C_{LP}$  is the peritectic limit and  $C_{\alpha p}$  is the peritectic point.  $C_x$  represents any alloy in the peritectic range with liquidus temperature  $T_L$ .

completely encapsulated with  $\alpha$ . Thereafter the three-phase contact required for equilibrium is no longer possible and the  $\alpha$ -phase continues to form at the expense of  $\beta$  by diffusion through the peritectic envelope. This is distinguished as the "peritectic transformation" [4] and can be described by the reactions



(at  $\alpha$ - $\beta$  interface)



(at  $\alpha$ -liquid interface) (2)

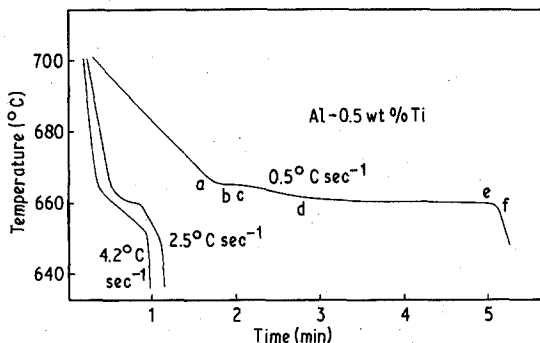


Figure 2 Cooling curves of a 0.5 wt % Ti peritectic alloy. The  $\beta$  liquidus temperature is above  $700^\circ\text{C}$ .

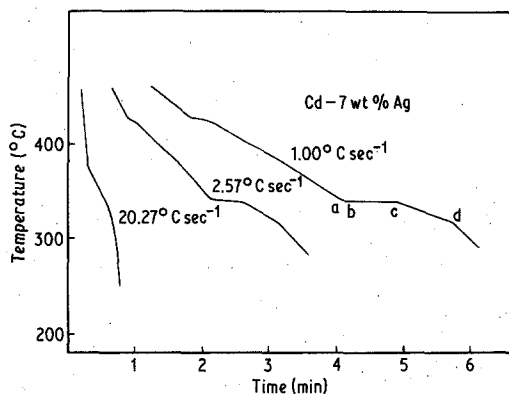
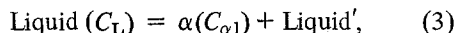


Figure 3 Cooling curves of a Cd-7 wt % Ag alloy. The  $\beta$  liquidus inflections are evident above  $400^\circ\text{C}$  for the 1.00 and  $2.57^\circ\text{C sec}^{-1}$  cooling curves.

where  $[B]$  represents atoms of component  $B$  diffusing outwards through the peritectic envelope. The transformation continues as temperature falls from  $T_P$  towards  $T_A$ . The cooling curve arrest  $bc$  has been interpreted [6] as recording the peritectic reaction, with  $cd$  (and  $de$ ) recording the subsequent transformation.

But the reaction and transformation must compete with a third freezing mode, which is direct crystallization of  $\alpha$ -phase from the melt. For non-peritectic alloys this can be described by



where Liquid' represents depletion of the liquid in component  $B$ . The same reaction can occur in the peritectic range at temperatures above  $T_P$  when the temperature falls below the metastable extension of the  $\alpha$  liquidus, for example, below  $C'_L$ . It has been shown for Al-Ti alloys [6] that there is a critical cooling rate above which  $\beta$ -phase

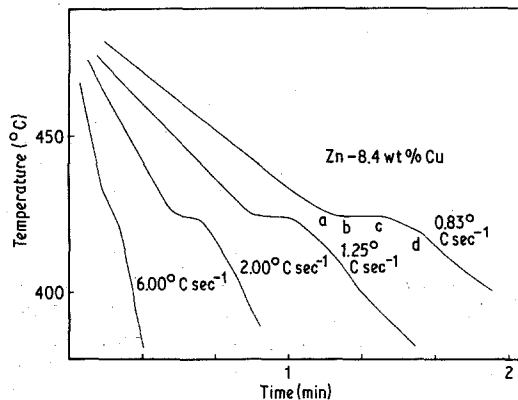


Figure 4 Cooling curves of a Zn-8 wt % Cu alloy. The  $\beta$  liquidus is above  $500^\circ\text{C}$ .

nucleation is completely suppressed in favour of  $\alpha$ -phase. Suppression becomes more difficult with increasing solute content, but is still achievable at compositions equivalent to  $C_x$ . Nucleation of  $\alpha$ -phase below the metastable liquidus should occur even more readily in the presence of primary  $\beta$ , since the remaining melt is enriched in  $A$  and the  $\beta$  surfaces are more likely than not to catalyse  $\alpha$  nucleation. Hence  $\alpha$ -phase nucleation is not dependent on the peritectic reaction, and crystallization of  $\alpha$  can occur above the peritectic temperature,  $T_p$ .

### 3. Apparent peritectic arrest

If we regard partial suppression of the primary  $\beta$ -phase as equivalent to lowering the  $\beta$  liquidus line [1], the suppressed  $\beta$  liquidus will cut the  $\alpha$  liquidus at a point such as  $C'_L$ . Liquid of composition  $C'_L$  is then saturated with respect to solid  $\alpha$  of composition  $C'_\alpha$  and nucleation can follow at some lower temperature which can be above  $T_p$ . In our experiments the beginning of  $\alpha$  nucleation was identified with the point  $a$  (Figs 2 and 3) at which a deviation from the liquid cooling curve was first observable. Point  $a$  corresponds to a nucleation temperature  $T_N$  which is followed by a near-horizontal arrest  $bc$  at temperature  $T' > T_p$ . Table I lists the observed tempera-

tures for these points for several alloys, including a Zn-Cu alloy (Fig. 4). The table shows that the apparent peritectic arrest was elevated above the equilibrium peritectic temperature by an amount  $(T' - T_p)$  which increased as cooling rate increased.  $T_N$  also rises with increasing cooling rate. The effect was that  $(T_N - T')$  also increased with cooling rate, despite the simultaneous increase in  $T'$ .

If the cooling rate is slow enough to maintain equilibrium the liquid composition must follow the  $\beta$  liquidus and remain unsaturated with respect to  $\alpha$  until the temperature falls to  $T_p$  with melt composition  $C_{Lp}$ . Nucleation of  $\alpha$  could then occur only at or below  $T_p$  and for this reason it was anticipated that negative values of  $(T_N - T_p)$  would be obtained at very slow cooling rates. No such undercooling was observed, from which it is concluded that some depression of the  $\beta$  liquidus results from even the slowest cooling rate used.

The transition from  $ab$  to  $bc$  was always smooth with no undercooling or recalescence at  $b$ . This suggests that, for each of the alloys examined, the pre-existing  $\beta$ -phase is an efficient nucleant for  $\alpha$ . (This would help to explain the failure to observe negative values of  $T_N - T_p$ .) Once formed, the  $\alpha$  nuclei on  $\beta$  surfaces would grow initially by the peritectic reaction (Equation 1). This three-phase

TABLE I Variation with cooling rate of  $\alpha$  nucleation temperature ( $T_N$ ) and apparent peritectic arrest temperature ( $T'$ ). ( $T_N$  is point  $a$ , and  $T'$  is point  $b$  in Figs 2 to 4.)

Liquid cooling rate, ( $^{\circ}\text{C sec}^{-1}$ )	Nucleation temperature, $T_N$ ( $^{\circ}\text{C}$ )	Peritectic arrest temperature, $T'$ ( $^{\circ}\text{C}$ )	Nucleation interval, $(T_N - T')$ ( $^{\circ}\text{C}$ )	Superheat, $(T' - T_p)$ ( $^{\circ}\text{C}$ )
Cd-7 wt % Ag (= $C_{\alpha p}$ ). Peritectic point = 7 wt % Ag, 343 $^{\circ}\text{C}$				
0.3	344	343	1	0
2.6	346	344	2	1
3.4	349	347	2	3
4.9	351	349	2	6
Cd-8.5 wt % Ag (hyperperitectic).				
1.0	344	343	1	0
4.8	351	349	2	6
5.7	354	351.5	2.5	8.5
Zn-8.4 wt % Cu (hyperperitectic). Peritectic point = 2.7 wt % Cu, 424 $^{\circ}\text{C}$				
0.8	425	424.8	0.2	0
1.3	427.5	424.5	3.0	0
2.0	429	424	5	0
6.0	443	429	14	5
Al-0.5 wt % Ti (hypoperitectic). Peritectic point = 1.15 wt % Ti, 665 $^{\circ}\text{C}$				
0.5	666.25	665	1.25	0
2.5	666			
4.2	667.2			

reaction is extremely fast and encapsulation of all particles of the  $\beta$ -phase could be complete while the average thickness of the  $\alpha$  envelope is still very small, perhaps only a few atoms thick. The amount of solid formed during the reaction is therefore very small and cannot be expected to contribute sufficient latent heat to maintain a horizontal thermal arrest. It is therefore suggested that the primary source of latent heat to maintain the near-horizontal arrest  $bc$  is the peritectic transformation (Equation 2), in which  $\alpha$  grows at the expense of  $\beta$  by diffusion through the peritectic envelope. The temperature falls from  $b$  to  $c$  as the melt composition changes down the metastable  $\alpha$  liquidus.

#### 4. Transformation versus direct precipitation

Once  $\alpha$ -phase is present, further growth is not dependent on dissolution of the  $\beta$ -phase. Alpha can form directly from the melt by Reaction 3, with the liquid composition changing down the liquidus. Reaction 3 can occur above and below  $T_p$  and competes with the peritectic transformation. The two reactions are indistinguishable metallographically in a randomly frozen sample, but their relative rates at any stage of freezing can be predicted by a diffusion analysis. It was shown in [4] that, for the Cd–Cd<sub>3</sub>Ag alloys, the transformation dominates whereas, for Al–Al<sub>3</sub>Ti, most of the  $\alpha$  is formed by direct precipitation from the melt. Because the  $\alpha$  formed via either process, transformation or direct precipitation, follows the same solidus line, it can be assumed that the amount of latent heat emitted is proportional to the amount of  $\alpha$  formed regardless of the process producing the  $\alpha$ . Hence the shape of the cooling curve at any time interval is related to the dominating  $\alpha$ -formation process.

In Fig. 5 the rate of transformation is plotted for a Cd–Ag alloy as  $V_T$ . (In [4]  $V_T$  was expressed as  $d\Delta x/dt$ , where  $\Delta x$  is the increase in thickness of the peritectic envelope in time period  $t$ .)  $V_T$  is initially rapid, while the envelope is thin, but decreases as the envelope thickens. By comparison, the rate of direct precipitation,  $V_C$ , will be essentially constant, because diffusion conditions between liquid and the  $\alpha$  surface change only with temperature. It is proposed that the rate of latent heat emission over the range  $bc$  is dominated by  $V_T$  and that the change in slope at  $c$  occurs when  $V_T < V_C$ , so that  $V_C$  dominates in the range  $cd$ .

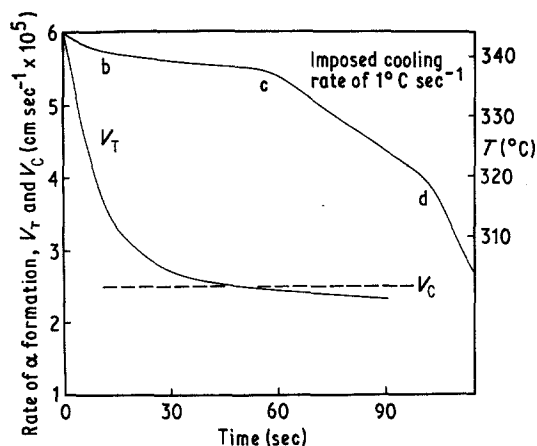


Figure 5 A Cd–Ag cooling curve (represented in the top of the figure) was used to calculate  $V_T$  according to [4].  $V_T$  and  $V_C$  are plotted against time after  $\alpha$  nucleation.  $V_T$  predominates up to the point where the cooling curve changes slope (i.e., at  $t = 60$  sec). The value of  $V_T$  at this point is equal to  $V_C$  which then predominates as  $V_T$  continues to drop.

In Fig. 5  $V_T$  was calculated as in [4] with the aid of one of the cooling curves of Fig. 3, which is superimposed in Fig. 5. If  $V_T$  becomes equal to  $V_C$  at point  $c$ , approximately 60 seconds after nucleation of  $\alpha$ , then the constant rate  $V_C$  is predicted to be  $2.5 \times 10^{-5} \text{ cm sec}^{-1}$ . This compares favourably with the value of  $2.7 \times 10^{-5} \text{ cm sec}^{-1}$  measured [4] for the same alloy solidified unidirectionally at a rate equivalent to  $1^\circ \text{ C sec}^{-1}$ .

In Fig. 3 the arrest  $bc$  becomes shorter at higher cooling rates and is absent at  $20.3^\circ \text{ C sec}^{-1}$ . This is typical behaviour, see also Figs 2 and 4, and indicates that  $V_C$  increases with cooling rate more rapidly than does  $V_T$  so that, with each increase in cooling rate, the peritectic transformation is interrupted at an earlier stage.

#### 5. Al–Al<sub>3</sub>Ti

The cooling curves for Al–Al<sub>3</sub>Ti (Fig. 2) differ from those for Cd–Cd<sub>3</sub>Ag and Zn–Cu in showing the additional feature of the long plateau  $de$  which is observable at slower cooling rates. The plateau is almost isothermal at about  $660^\circ \text{ C}$ , which is approximately the solidification temperature of pure aluminium. The indication is that nearly all the dissolved titanium is removed from the liquid in the first stages of  $\alpha$  formation, over the range  $cd$ , whereas equilibrium freezing would require a steady fall in temperature as the liquid composition follows down the liquidus to a final composition  $C_L = C_{Lp}/k$  (where  $k$  is the partition

coefficient  $C_{\alpha p}/C_{Lp}$  and  $C_{Lp}$  is the composition of the last solid to form). However, the condition of equilibrium is that the solid  $\alpha$ -phase formed is at all times of uniform composition  $C_{\alpha 1}$  decreasing in solute content as temperature falls. In fact there must always be a composition gradient through the  $\alpha$  envelope to maintain Equation 2. Hence the average composition of the phase present at an intermediate temperature  $T_R$  will lie between  $C'_\alpha$  and  $C_{\alpha 1}$  with higher solute content than equilibrium. This could be represented by an effective solidus line displaced to the high solute side of  $C_\alpha$ , in complete analogy with the conventional non-equilibrium solidus line used in describing freezing of a single-phase alloy in a eutectic or single-phase system (e.g. [9]).

For the Cd–Cd<sub>3</sub>Ag system it has been shown [4] that diffusion through the peritectic envelope to satisfy Equation 2 occurs at a rate fast enough to permit the peritectic transformation to dominate the overall transformation ( $V_T > V_c$  in Fig. 5). Hence the composition gradient through the  $\alpha$  envelope is kept small and the displacement of the  $\alpha$  solidus must be negligibly small. Then the range  $cd$  in Fig. 3 represents a continuous composition change down the liquidus until final solidification of liquid near the equilibrium value of  $C_L = C_{Lp}/k$ . But for the Al–Al<sub>3</sub>Ti system the situation is reversed. Transformation by diffusion through the envelope is very slow relative to the rate of direct crystallization by Equation 3. It follows that the composition gradient through the  $\alpha$  envelope must remain high and the effective solidus line is displaced strongly to higher titanium contents. For the  $0.5^\circ\text{Csec}^{-1}$  cooling rate in Fig. 2 this depletion occurs over the range  $cd$ , after which the remaining liquid is almost pure aluminium and freezing is completed near the freezing point of aluminium over the range  $de$ . At higher freezing rates the rate of heat extraction exceeds the rate of latent heat evolution and the temperatures recorded bear little relationship to the equilibrium temperatures, although similar freezing sequences may be assumed. The sequence proposed for slow freezing rates conforms with the experimental observations of unidirectional solidification in [4]. In Al–Al<sub>3</sub>Ti alloys most of the  $\alpha$  was formed by direct crystallization from the melt (Equation 3) at a near-isothermal  $\alpha$ -liquid interface at a temperature near the freezing point of aluminium. For the Cd–Cd<sub>3</sub>Ag alloys most of the  $\alpha$  formed by thickening of the peri-

itectic  $\alpha$  envelopes while temperature fell continuously. Direct crystallization of  $\alpha$  played a minor part.

## 6. Depression or elevation of the peritectic arrest

In all the alloys studied in these experiments elevation of the arrest was observed consistently, i.e.,  $T' - T_p$  was always positive or zero and increased with cooling rate (Table I). These results appear to conflict with published reports [7, 8] of undercooling of the apparent peritectic arrest, i.e.,  $T' - T_p$  negative, but a single hypothesis can be used to explain both types of observation. The elevation phenomenon was related in Fig. 1 to a depression of the  $\beta$  liquidus, but it can also be expected that the  $\alpha$  liquidus would be depressed to a certain extent, as in Fig. 6. This is indicated by the results of Kerr *et al.* [6], which show that the temperature of  $\alpha$  nucleation was below the extended  $\alpha$  liquidus, to an extent increasing with increasing cooling rate. The same effect can be expected to extend to the equilibrium  $\alpha$  liquidus. Fig. 6 shows that, for a given depression of the  $\beta$  liquidus, a minor depression of the  $\alpha$  liquidus will leave  $T' - T_p$  positive, whereas a large  $\alpha$  depression can make  $T' - T_p$  negative.

The relative depression of  $\beta$  and  $\alpha$  liquidus lines can be affected both by the cooling conditions and by the efficiency of the  $\beta$  phase as a nucleant for  $\alpha$ . If a melt has been held just above the  $\beta$  liquidus, the furnace conditions can be such that the rate of heat extraction is initially low, minimizing the liquidus depression, but increases as  $T_p$  is approached, causing a larger depression of the  $\alpha$  liquidus. It is perhaps more probable that undercooling is observed when the  $\beta$ -phase is a poor nucleant for  $\alpha$ . Then substantial undercooling below the  $\alpha$  liquidus can be expected in order that impurity particles can nucleate the  $\alpha$ -phase. Sub-

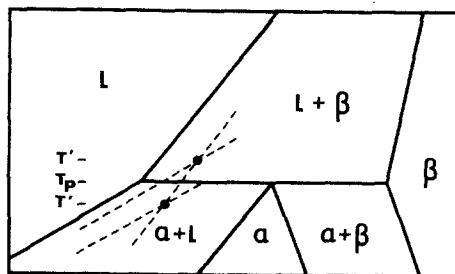


Figure 6 The effect of different amounts of depression of the  $\alpha$  and  $\beta$  liquidus lines on the elevation or depression of the peritectic arrest temperature.

sequent recalescence is probable, but this will not necessarily raise the temperature above  $T_p$ .

## 7. Conclusions

(1) Predictions that increasing cooling rates will result in increasing elevation of the peritectic arrest temperature are confirmed for Cd–Ag and Zn–Cu alloys.

(2) Cooling curve observations suggest that nucleation of the peritectic product above the equilibrium peritectic temperature is a normal occurrence at most cooling rates.

(3) The shape of peritectic cooling curves was related to the change in rates of  $\alpha$  formation during growth (i.e., latent heat generation is proportional to the amount of  $\alpha$  produced per unit time).

(4) Whether elevation or depression of the peritectic arrest occurs is dependent on the relative amounts of  $\alpha$  and  $\beta$  suppression during cooling (i.e., the result of the  $\alpha$  liquidus and  $\beta$  liquidus being depressed by varying relative amounts).

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