

# NON-EQUILIBRIUM SOLIDIFICATION IN A PERITECTIC SYSTEM

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## ABSTRACT

Lead-bismuth alloys were subjected to a wide range of non-equilibrium solidification rates and studied by standard optical and X-ray metallographic techniques. In the light of the results, a modified peritectic solidification mechanism has been suggested.

## INTRODUCTION

THE solidification of a liquid, through a peritectic reaction, *e.g.*,  $\alpha + L \rightarrow \beta$  in a binary system, has received very little attention despite the fact that this reaction is extremely common in metallic systems. The peritectic reaction has been recognized<sup>1</sup> as a means of effecting grain refinement in alloys and also as a method of growing intermetallic compounds with special properties. Description of the peritectic reaction given in most metallurgical text-books, with the exception of few,<sup>2,3</sup> are in terms of maintaining equilibrium conditions during the solidification process, a requirement that is almost impossible of fulfilment in practice. Recently, some peritectic systems have been studied<sup>4-7</sup> under non-equilibrium solidification conditions. With a view to understand the impact of the rate of solidification on the mechanism of peritectic reaction and also to explore the possibility of predicting the morphology of the constituents in alloys of a peritectic system solidifying under non-equilibrium conditions, we have embarked on some detailed solidification studies of the lead-bismuth system<sup>8</sup> featuring the peritectic reaction (Fig. 1). The preliminary results presented here concern solidification of three alloys, each under four different non-equilibrium cooling conditions.

## EXPERIMENTAL PROCEDURES AND RESULTS

Pb-Bi alloys of three compositions, *i.e.*, 15, 26 and 37 wt.% bismuth, one of them undergoing the peritectic reaction on cooling according to the phase diagram and the other two with compositions on either side of the peritectic horizontal, *i.e.*, one to the left of A and the other to the right of C in Fig. 1, were chosen for the present study. Lead and bismuth of more than 99.9% purity were used in preparing the charges. The loss in weight after melting was always negligible.

Many different techniques of melting and solidification were used in preparing the alloy specimens. Calculated amounts of the two metals were generally weighed out for 100 g.

charges and melted in corning glass tubes. The melts were thoroughly agitated to effect homogenization and then the tubes were cooled in a furnace from 350°C. to room temperature. Melts prepared in the above manner were also cooled in a jet of compressed air, directed at the bottom of the glass tubes. In another variation of this technique, 100 g. charges of the required compositions were sealed in evacuated pyrex glass capsules, heated in a furnace up to 350°C., homogenized by thorough mixing of the melt and eventually chilled in water.

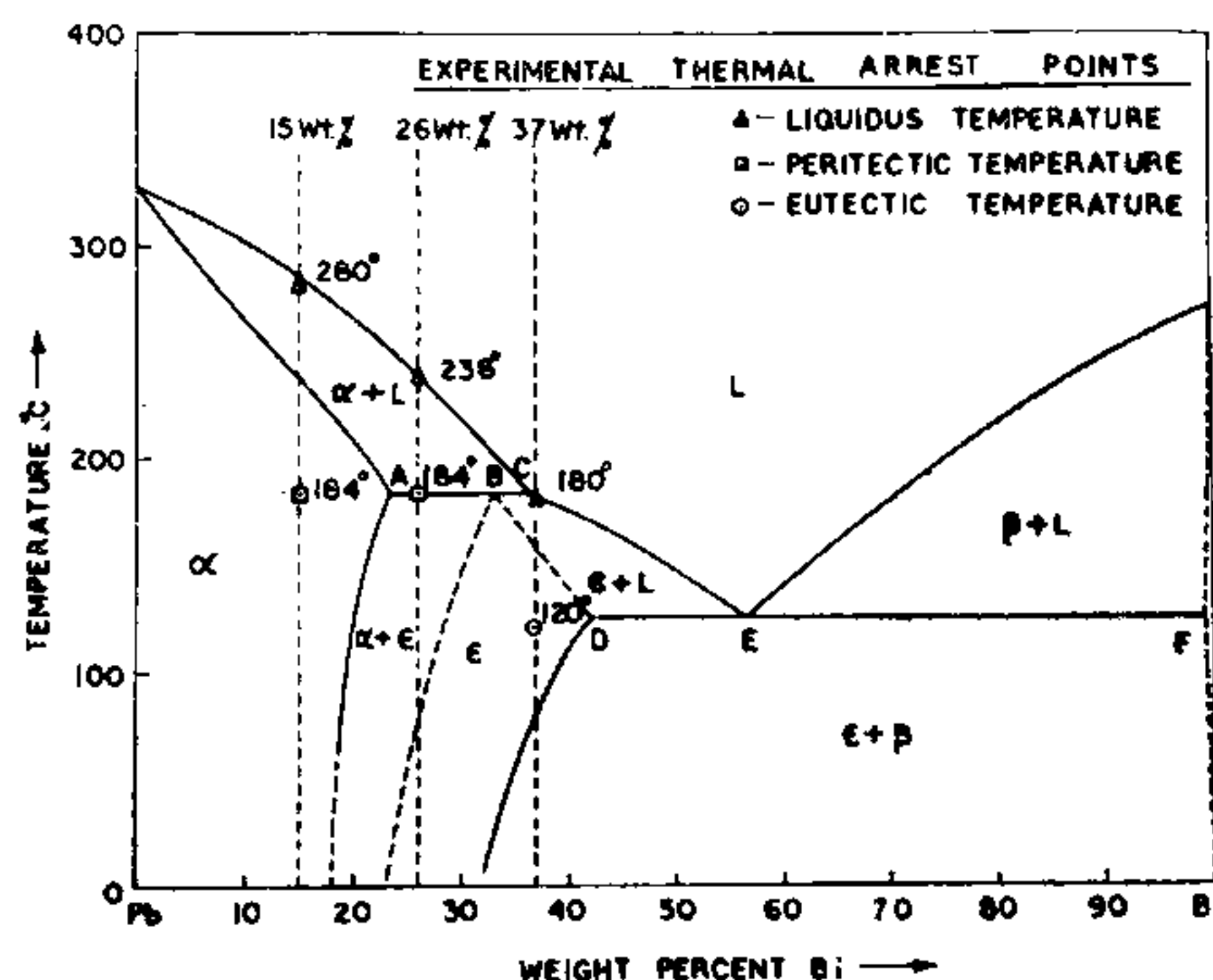


FIG. 1. Phase diagram of Pb-Bi system indicating experimental thermal arrest points. (Equilibrium Peritectic Horizontal: Temperature 184°C.; Compositions—A, 23.5%; B, 33.4%; C, 36.2%. Equilibrium Eutectic Horizontal: Temperature 125°C.; Compositions—D, 42.0%; E, 56.5%; F, 99.5%.)

The novel splat-cooling technique of extremely rapid quenching from the liquid state was also used in our studies. The apparatus employing the so-called gun technique was similar to the one, developed by Duwez and Willens<sup>9</sup> and has been described in detail elsewhere.<sup>10,11</sup> In each experiment about 20-30 mg. of the alloys prepared by the conventional melting technique were heated up to 350°C. in a graphite crucible, splat-atomized by a shock wave induced by nitrogen gas under high pressure and quenched on to a copper substrate.

Cylindrical samples were cut from the ingots solidified under different cooling rates. They were polished and examined metallographically, adopting the usual precautions for good surface finish and using a 5% aqueous solution of silver nitrate as etchant. In case of splat-cooling experiments, the very thin foils obtained by quenching did not require any metallographic preparation.

To identify and confirm the phases present, all samples were subjected to X-ray examination. Fine splat flakes were collected and mounted on a thin glass fibre with the help of 'Quick fix' to make suitable X-ray specimens. Similarly specimens were prepared from the fine powder obtained by filling the cylindrical samples. The Debye-Scherrer patterns were obtained, using a 114.6 mm. dia. Philips camera with nickel-filtered  $\text{Cu K}\alpha$  radiation. The observed interplanar spacings were compared with the calculated ones and thus the phases were identified.

To gain further understanding of the solidification processes under different cooling rates, thermal analysis was conducted on all the alloys. Required quantities of the two pure metals were weighed out for 500 g. charges and melted in an alumina crucible placed in a resistance-heated furnace. Cooling curves were obtained on furnace cooling with the aid of a continuous temperature recorder, using standard chromel-alumel thermocouples enclosed in stainless steel sheaths.

The thermal arrest points obtained in case of each alloy are shown in Fig. 1. A summary of the microstructural and X-ray observations are given in Table I. The departure from equilibrium is pronounced for all rates of solidification employed in the present work.

as per phase diagram (Fig. 1). As the temperature further falls, more of  $\alpha$  will solidify either through growth of the original nuclei or through formation of more  $\alpha$  crystals. In the temperature range from the liquidus to the peritectic reaction, the amount of the primary  $\alpha$  will continue to increase and its composition change according to the solidus as modified for the non-equilibrium conditions. During the process of solidification, the  $\alpha$  crystals will reject bismuth at the interface and thus, as the temperature falls, the composition of the liquid adjacent to  $\alpha$  crystals will become correspondingly richer in bismuth. Thus there will be a layer of constitutionally super-cooled liquid, surrounding the primary  $\alpha$  crystals. The above condition of under-cooling, ahead of the interface, may be considered suitable for producing a dendritic morphology (Figs. 2, a, b). The various branches of the  $\alpha$  dendrites will grow until inhibited in the lateral direction by other similar dendrites. The morphology of the  $\alpha$ -phase will, however, depend on the temperature gradient and the solidification rate. If the temperature gradient is steep and the solidification is high, there will only be a narrow region of under-cooled liquid into which the dendrites can grow. The time allowed for growth in the lateral direction will be short and this will result in fine dendrites. It can be seen that dendrites are much finer in the splat-cooled structure (Fig. 2, b) than in the air-cooled one (Fig. 2, a).

When more and more of  $\alpha$  crystals are formed during solidification and the liquid between these crystals becomes more and more enriched in bismuth, the composition of the liquid may well reach C (Fig. 1). In such an extreme non-equilibrium situation,  $\epsilon$  crystals may

TABLE I  
Microscopic and X-ray evidence for the phases in lead-bismuth alloys

Solidification condition	Pb-15 wt. % Bi alloy		Pb-26 wt. % Bi alloy		Pb-57 wt. % Bi alloy	
	Microscopic evidence	X-ray evidence	Microscopic evidence	X-ray evidence	Microscopic evidence	X-ray evidence
Equilibrium cooling	..	$\alpha$	$\epsilon$	$\epsilon$	$\epsilon + \beta$	$\epsilon + \beta$
Furnace cooling	..	$\alpha + \epsilon$	$\alpha + \epsilon + E$	$\alpha + \epsilon + \beta$	$\epsilon + E$	$\epsilon + \beta$
Air cooling	..	$\alpha + \epsilon$	$\alpha + \epsilon$	$\alpha + \epsilon + \beta$	$\epsilon + E$	$\epsilon + \beta$
Water cooling	..	$\alpha + \epsilon$	$\alpha + \epsilon$	$\alpha + \epsilon + \beta$	$\epsilon + E$	$\epsilon + \beta$
Splat cooling	..	$\alpha + \epsilon$	$\alpha + \epsilon$	$\alpha + \epsilon + \beta$	$\epsilon + \beta$	$\epsilon + \beta$

$\alpha$ , Solid solution of bismuth in lead;  $\epsilon$ , Intermediate phase; E, Eutectic mixture of  $\epsilon$  and  $\beta$ ;  $\beta$ , Solid solution of lead in bismuth.

#### DISCUSSION OF RESULTS

(i) *Solidification of Lead-15 wt.% Bismuth Alloy.*—When this alloy is cooled to its liquidus temperature, nucleation of  $\alpha$  crystals will occur

nucleate and grow as a result of the peritectic reaction and/or direct solidification. The resulting solid would then be two-phase, consisting of  $\alpha$  and  $\epsilon$ . On further cooling to room



temperature, precipitation of  $\epsilon$  may also take place within the  $\alpha$  crystals. This is precisely what we have observed in our alloys on increasing the rate of solidification.

the peritectic temperature, the  $\alpha$ -phase may react with the liquid to give the peritectic product  $\epsilon$ . But this reaction will occur only to a very limited extent, unless very long times are

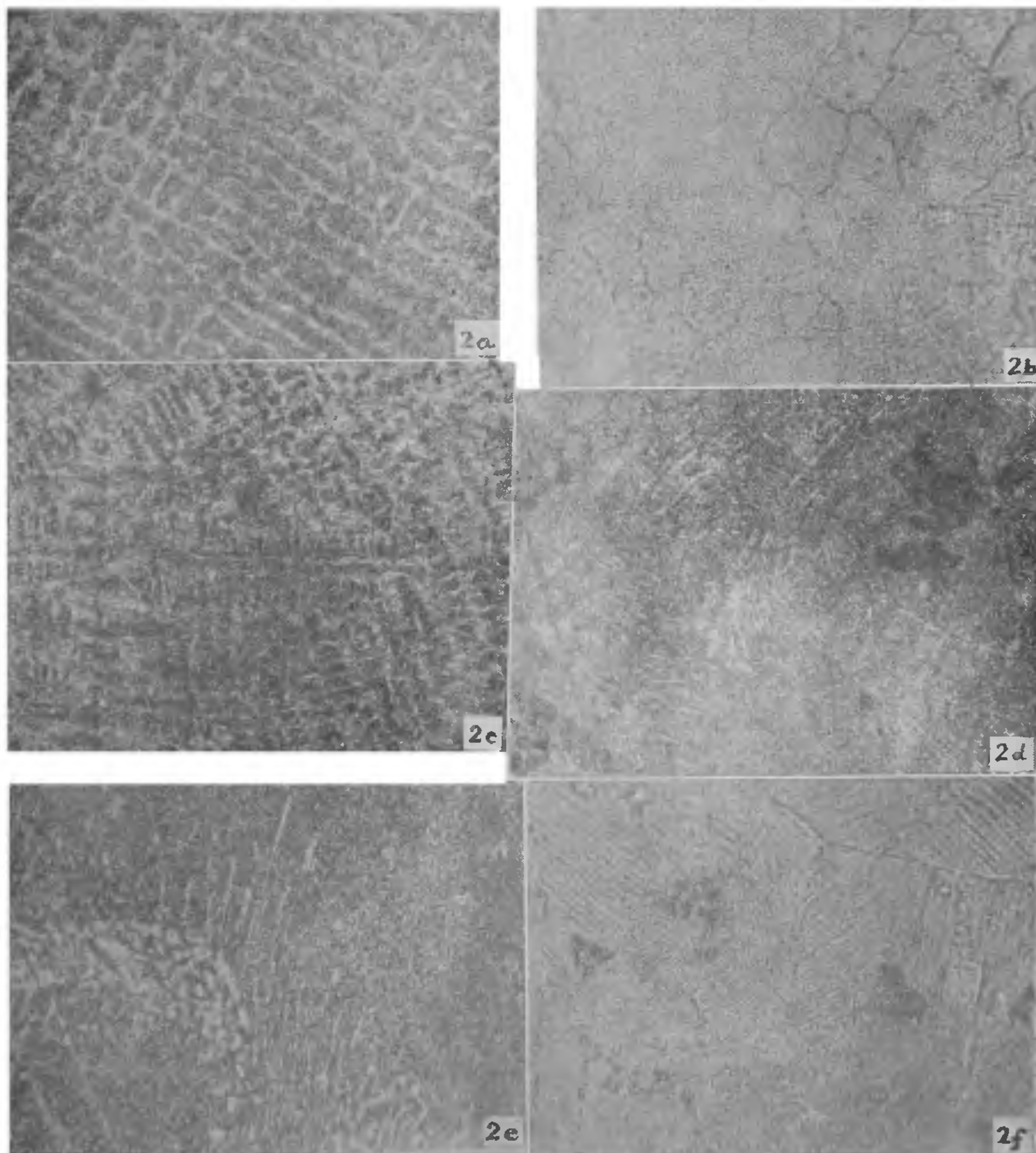


FIG. 2. Photomicrographs of Pb-Bi alloys. (a) 15 wt.% Bi, air-cooled,  $\times 200$ ; (b) 15 wt.% Bi, splat-cooled,  $\times 750$ ; (c) 26 wt.% Bi, furnace-cooled,  $\times 50$ ; (d) 26 wt.% Bi, furnace-cooled,  $\times 200$ ; (e) 37 wt.% Bi, furnace-cooled, 350; (f) 37 wt. % Bi, splat-cooled,  $\times 750$ .

(ii) *Solidification of Lead-26 wt.% Bismuth Alloys.*—In case of this alloy, on cooling from the molten state to nearly the peritectic temperature, the process of solidification will be more or less the same as discussed above. At

available during freezing and subsequent cooling to convert the  $\alpha$ -phase completely to the  $\epsilon$ -phase. In practice, therefore, the  $\alpha$ -phase will persist even in the peritectic alloy, although it is not an equilibrium phase (Fig. 2, c). Because



of the limited nature of the reaction, it is quite possible that on further cooling some of the unreacted liquid may directly precipitate  $\epsilon$ -phase, thereby increasing the bismuth content of the remaining liquid beyond C. In such an extreme case, the liquid will eventually solidify as a eutectic mixture of  $\epsilon$  and  $\beta$  in some areas. Even in furnace-cooled samples, such a eutectic structure was actually seen by us in some areas (Fig. 2, d).

(iii) *Solidification of Lead-37 Wt.% Bismuth Alloy.*—In this case, under equilibrium cooling, the solid at room temperature should consist essentially of the  $\epsilon$ -phase with some precipitation of  $\beta$  in each  $\epsilon$  grain. But under non-equilibrium conditions, it is possible that, due to the very rapid rise in the bismuth content of the liquid, as freezing approaches completion, a small portion of the liquid may reach the eutectic composition and solidify as the eutectic. The structure at room temperature will then consist of grains of  $\epsilon$ , along with the eutectic mixture of  $\epsilon$  and  $\beta$  at the grain boundaries (Fig. 2, e).

In splat-cooled samples of all compositions, a two-phase dendritic and/or a cellular structure would be observed under the optical microscope (Figs. 2, b and f). Our results agree with those of Borromee-Gautier *et al.*<sup>5</sup> in that no new phases were observed in the composition range studied. The single-phase structure, obtained in some cases by them,<sup>5</sup> may be explained as due to the facts that their splat-cooling rates were perhaps faster and all their studies were carried out at  $-190^{\circ}\text{C}$ . and not at room temperature, as in our case.

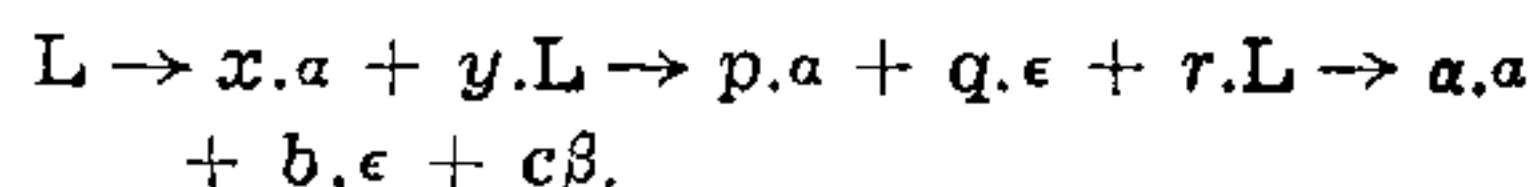
(iv) *The Mechanism of Peritectic Solidification.*—Under equilibrium coolings, the  $\epsilon$ -phase is expected to form in alloys of the peritectic composition range of the Pb-Bi system as a result of the following simple peritectic reaction:



The reaction product  $\epsilon$  will form at the interface between  $\alpha$ -phase and the liquid, enveloping thereby the  $\alpha$  crystals. As a result, a ring structure should generally be obtained. The present study shows, however, that no such structure forms as a result of the peritectic reaction, in cases of departures from ideal equilibrium conditions. Obviously, the above reaction occurs in practice only to a very limited degree, the extent of the reaction depending very much on the cooling conditions. With even furnace cooling, this reaction seems to occur to a very small extent. At such

cooling rates, one may or may not observe the thermal arrest point. In case of furnace cooling, the thermal arrest point was indeed observed, though not as marked as the eutectic arrest point. Under more or less similar conditions, no ring structure was observed under the microscope. It can thus be concluded that for all practical purposes the conventional peritectic reaction hardly takes place and can be ignored.

According to our observations, at the peritectic temperature,  $\epsilon$  does not seem to form by the peritectic reaction between  $\alpha$  and the liquid, but rather forms by direct precipitation from the liquid enriched in bismuth, as the alloy is cooled through the peritectic temperature. Because of the direct precipitation of  $\epsilon$ , the remaining liquid may well get enriched in bismuth content even beyond C (Fig. 1) and thus give rise to a eutectic product on further cooling. Thus, under non-equilibrium cooling conditions, the entire peritectic solidification may be postulated to take place in the following manner:



where  $x$  and  $y$ ,  $p$ ,  $q$  and  $r$  as well as  $a$ ,  $b$  and  $c$  represent mole fractions that will vary according to the cooling condition as well as the alloy composition. In practice, the values of  $x$ ,  $p$  and  $a$  seem to be of the same order.

The mechanism proposed above explains the presence of the eutectic (Fig. 2, d) in hypoperitectic alloys, as clearly established metallographically and verified by X-ray analysis in the present work. Such a peritectic solidification mechanism should be helpful in rationalising non-equilibrium solidification phenomena in alloys of peritectic systems.

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