# The ε-phase in rapidly solidified ferrous alloys

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An Fe–1.9 wt% Si–4.2 wt% C alloy has been rapidly quenched from the melt in a controlled-atmosphere "gun" splat-cooling device to produce material consisting predominantly of the hexagonal close-packed e-phase. The techniques of X-ray diffraction, scanning and transmission electron microscopy, and differential thermal analysis have been used to study the nature of the e-phase and its decomposition during heat treatment. The presence of the metastable e-phase could not be accounted for as the transformation product of a low stacking-fault energy austenite, and it appears to be formed directly from the liquid state. It has a complex and variable microstructure, which ranges from elongated, relatively featureless grains in the most rapidly-cooled areas to highlyfaulted and twinned structural units containing precipitate particles. The e-phase undergoes a two-stage decomposition process upon heating, but the first stage does not appear to involve the formation of martensite and e-carbide, which has been the hitherto accepted reaction. As an alternative it is suggested that the e-phase may decompose by a spinodal reaction.

# 1. Introduction

The formation of metastable hexagonal closepacked (hcp)  $\epsilon$ -phase in splat-cooled Fe-C and Fe-C-X alloys, where X is a substitutional alloy. ing element, has been reported a number of times [1-9].

In their pioneering study, Ruhl and Cohen [2] deduced that the composition of the  $\epsilon$ -phase ranges from about 3.8 to 4.8 wt% carbon, whilst subsequent work has defined the limits of existence of this phase as  $Fe_6C$  and  $Fe_3C$  [7]. The volume fraction of  $\epsilon$ -phase retained upon splatcooling was found to increase with carbon content and cooling rate, and to increase markedly with silicon content, reaching a maximum of 97% at a composition of Fe-1.9 wt% Si-4.5 wt%C. Ternary additions of nickel and manganese had a similar but not so dramatic effect as silicon, whereas cobalt, chromium and ruthenium had little effect in increasing the yield of  $\epsilon$ -phase above that in corresponding Fe-C compositions. This led to the conclusion that  $\epsilon$ -phase retention was related to the amount of carbon in solution, so that the presence of a third element which inhibited carbide formation would enhance  $\epsilon$ -phase formation [2].

From a comparison of the atomic volume of

 $\epsilon$ -phase with the atomic volumes of other related hcp phases found in ferrous systems, the former has been shown to be more closely related to  $\epsilon$ iron, a phase normally found only at high pressure [10], than to  $\epsilon$ -carbide or  $\epsilon$ -nitride. More recently the occurrence of hcp  $\epsilon$ -phase instead of facecentred cubic (fcc) austenite in splat-cooled hypereutectic irons has been attributed to a decrease in the stacking fault energy of the fcc phase caused by the presence of carbon in solution [8]. However, no evidence was presented to support this contention. The decomposition of  $\epsilon$ -phase upon heating has been described by a twostage process, involving the formation of martensite plus  $\epsilon$ -carbide after 1 h at 140 to 200° C and then ferrite plus cementite after 1 h at 330 to 460° C [2].

All of these investigations on the  $\epsilon$ -phase have concentrated upon alloys with high carbon levels, typical of cast irons, since it has always been assumed that  $\epsilon$ -phase will form only when there are very large amounts of carbon in solution. However, it has been shown more recently [9] that  $\epsilon$ -phase may form in a Fe-Ti-C alloy at an overall carbon level of 0.5 wt%, despite the earlier observation [2] that elements which tend to deplete

Alloy	ε-phase		Austenite (y)	Reference	
	a(Å)	c(Å)	c/a	a(Å)	
Fe-1.9 wt% Si-4.2 wt%C*	2.611-2.629	4.308-4.323	1.644-1.650	3.623-3.638	This work
Fe-1.5 wt% Si-4.2 wt%C	2.622	4.318	1.646	-	[1]
Series of Fe–Si–C <sup>†</sup> alloys	2.623-2.653	4.307-4.354	1.641-1.646	3.617-3.638	[2]

TABLE I Lattice parameters in splat-cooled Fe-Si-C alloys

\*Data for this alloy are the extreme values from four splat production experiments.  $\frac{1}{2}$ 

<sup>†</sup>Si content varied from 0.34 to 3.27 wt%; C content varied from 3.83 to 4.99 wt%.

the carbon content of austenite (e.g. titanium) retard  $\epsilon$ -phase formation.

In view of this uncertainty, and the fact that no metallographic study has been made of  $\epsilon$ -phase or its decomposition process, this investigation has been carried out to evaluate some of the unresolved problems associated with  $\epsilon$ -phase formation and decomposition. Ruhl and Cohen [2] found that the volume fraction of  $\epsilon$ -phase formed was at a maximum in an Fe-1.9 wt% Si-4.5 wt%C alloy, and therefore an alloy close to this composition was chosen for this study.

# 2. Experimental procedure

The details of the experimental procedure used in this investigation closely followed those of other studies carried out on splat-cooled ferrous alloys [9, 11, 12]. An Fe–Si–C ingot was prepared from high-purity constituent elements in an argon arc furnace as described previously [11]. The ingot was then sealed in a silica capsule under a partial pressure of argon and homogenized for 6 h at  $1100^{\circ}$  C. The results of chemical analyses carried out on turnings taken from both ends of the ingot are: C–4.20 wt%, Si–1.90 wt%.

The surface of the ingot was cleaned by filing, and small pieces weighing approximately 0.25 g were melted and solidified in a controlledatmosphere gun splat-cooling apparatus [13]. Xray diffraction, scanning and transmission electron microscopy, and differential thermal analysis were carried out on both as-splatted and heat-treated material, as described previously [11].

# 3. Results

# 3.1. Splat-cooled material

# 3.1.1. X-ray diffraction analysis

Debye-Scherrer powder photographs were taken of material from four splat-cooling runs with this alloy, and in all cases the  $\epsilon$ -phase was predominant. Very small amounts of austenite were also detected. The lattice parameters of the hexagonal  $\epsilon$ phase were determined with a standard computer program using Cohen's method of least squares. Since 12 fairly sharp lines of this phase were present on each film, the lattice parameters of  $\epsilon$  for any given sample could be determined to within approximately  $\pm 0.001$  Å. The accuracy of the austenite lattice parameter was limited to  $\pm 0.011$  Å by the fact that only three austenite reflections could be detected on the Debye-Scherrer films.

Table I lists the lattice parameter data, and for comparison shows the results obtained by Ruhl and Cohen [1, 2]. Considerable spread is evident in the lattice parameters of  $\epsilon$ -phase from the four splat production experiments with the one alloy in the present work. Since the cooling rate attained in any one experiment cannot be closely controlled, the range of values is probably indicative of solute content variations produced by differing rates. The lattice parameters for each alloy published by Ruhl and Cohen were determined apparently from only one experiment. An even broader spread of values may have been obtained had these workers adopted a similar technique to that used in the present work, and calculated lattice parameters for several independent runs of each alloy.

# 3.1.2. Metallographic examination.

Characterization of the microstructural features of the  $\epsilon$ -phase was inconclusive because of the many different forms observed. The surfaces of relatively large splats examined by scanning electron microscopy showed bundles of lath-like features in the unpolished, unetched condition (Fig. 1a), whilst electropolished and etched flakes (Fig. 1b) exhibited a dendritic mode of growth with, apparently, superimposed crystallographic growth of the structural units surrounding the dendrites. The observations described below indicate that these structural units may be twins within the  $\epsilon$ -phase.

Unthinned flakes contained elongated grains of.  $\epsilon$ -phase (Fig. 2a) in the thinnest areas observed in the transmission electron microscope. Such regions



Figure 1 Scanning electron micrographs of splat-cooled Fe-1.9 wt% Si-4.2 wt%C alloy: (a) unprepared surface showing bundles of laths; (b) electropolished and etched surface illustrating dendritic growth.

closely resembled the very thin areas of ferrite observed in other splat-cooled alloys, where growth had obviously occurred in the plane of the foil [9, 11, 12]. It is evident that such a mode of solidification is a general feature of the fastestcooled areas of splat-cooled material [14]. Other unthinned regions revealed more complicated morphologies of the  $\epsilon$ -phase. Among the distinctive structures observed were twins in a highly faulted matrix, in which there appeared to be fine rows of precipitate particles within the twins (Fig. 2b). In other areas it appeared that the twins resembled some type of martensitic phase (Fig. 2c). The breadth of the twins varied markedly from area to area, and in unthinned foils broad twins such as those in Fig. 2b and c were often present, whilst in other areas much narrower twins, all lying in the one direction in a given grain, were common (Fig. 3a and b).

A further phenomenon found in this alloy was the existence of two non-crystalline phases in the thinnest parts of some foils. The principal details have been described previously [4], and where both crystalline and non-crystalline phases were observed in the same area, the crystalline material was invariably grains of faulted  $\epsilon$ -phase, as confirmed by Boswell and Chadwick [5].

# 3.2. Splat-cooled and heat-treated material 3.2.1. Differential thermal analysis and X-ray diffraction analysis

Several samples of the splat-cooled material were heated at a rate of  $20 \text{ K min}^{-1}$  in a differential thermal analysis apparatus, and in all instances two

exothermic peaks were detected between ambient temperature and 600° C. A typical thermogram is shown in Fig. 4. Specimens heated to 205° C (just above the first peak), to  $420^{\circ}$  C (below the second peak), and to  $560^{\circ}$  C (above the second peak) were examined by X-ray diffraction. Although the X-ray powder patterns of the splat-cooled material contained relatively sharp  $\epsilon$ -phase lines with little broadening and low background intensities, all photographs of material heated past the first peak exhibited very pronounced broadening and exceedingly high background intensities. This made identification of the phases present very difficult. Table II presents the X-ray results from samples of material from one particular experimental run, showing the *d*-spacings and relative intensities of the reflections present after splat-cooling, and heating to 205° C and 420° C. Heating to 560° C, past the second peak, resulted in the complete disappearance of all the phases shown in the table, and in the formation of ferrite and cementite.

Ruhl and Cohen [2] studied the decomposition of  $\epsilon$ -phase by heating samples for 1 h at various temperatures and subsequently examining them by X-ray diffraction. They detected decomposition of  $\epsilon$ -phase in the temperature range 140 to 200° C and, although they could make no precise identification of the phase changes because of the broadness and diffuse nature of the reflections, they explained their results on the basis of the reaction:

#### $\epsilon$ -phase $\rightarrow \epsilon$ -carbide + martensite.

Between 200 and  $300^{\circ}$  C no further changes were detected but between 330 and  $460^{\circ}$  C they







Figure 2 Different morphologies of  $\epsilon$ -phase in unthinned foils. Transmission electron micrographs: (a) elongated grains; (b) twins, containing precipitate particles, in a faulted matrix; (c) twins in a faulted matrix.

observed:

 $\epsilon$ -carbide + martensite  $\rightarrow$  ferrite + cementite.

In order to confirm whether the present results were consistent with this particular two-stage process, lattice parameters were calculated for the hcp decomposition product of the  $\epsilon$ -phase designated  $\epsilon'$ -phase in Table II. The results of this calculation are shown in Table III, together with the parameters of the as-splatted material and



Figure 3 Finely-twinned  $\epsilon$ -phase in an electropolished foil. Transmission electron micrographs: (a) bright-field; (b) dark-field.

TABLI	E II Com	parison	of interplana	r spacings	and	relative	intensities	of	the	phases	in the	splat-	cooled	Fe-1.	9 wt%
Si-4.2 w	vt%C alloy	after s	plat-cooling a	nd after h	eatin	ig to 205	5 and $420^{\circ}$	С							

Splat-cooled			Heated t	o 205° C		Heated to 420° C			
<i>d</i> (Å)	Relative intensity	Phase	d(Å)	Relative intensity	Phase	<i>d</i> (Å)	Relative intensity	Phase	
2.273	s	e	2.326	m	ε'	2.337	m	ε'	
2.156	S	e	2.135	S	$\epsilon'$	2.170	m	$\epsilon'$	
2.092	m	γ	2.092	m	$\gamma$	2.091	m	γ	
			2.043	vs	$\alpha', \epsilon'?$	2.055	vs	$\alpha', \epsilon'?$	
2.011	vs	e				2.027	S	$\alpha', \epsilon'?$	
1.815	w	$\gamma$	1.814	w	γ	1.814	w	γ	
1.566	S	$\epsilon$	1.581	m	$\epsilon'$	1.591	m	$\epsilon'$	
						1.435	vw	α΄	
1.314	S	$\epsilon$	1.330	vw	$\epsilon'$	1.344	w	$\epsilon'$	
1.280	vw	γ	1,283	vw	γ	1.284	vw	γ	
1.261	S	E	1.219	m	$\epsilon'$	1.229	w	$\epsilon'$	
			1.158	m	α'	1.169	m	α'	
1.138	VW	$\epsilon$				1.145	vw	$\epsilon'$	
1.123	8	e	1.124	vw	ε'	1.126	VW	$\epsilon'$	
1.100	S	ε	1.093	w	γ	1.092	w	γ	
1.080	w	e	1.047	vw	γ				
1.007	m	$\epsilon$				1.010	vw	$\alpha'$	
0.976	m	e							

vs = very strong, s = strong, m = medium, w = weak, vw = very weak,  $\epsilon = \epsilon$ -phase,  $\gamma$  = austenite,  $\alpha'$  = martensite,  $\epsilon'$  = decomposition product of  $\epsilon$ .

 $\epsilon$ -carbide [15]. It appears that the  $\epsilon'$  decomposition product is not  $\epsilon$ -carbide, and the trend in the *d*-spacings in Table II and the lattice parameters and c/a ratios in Table III indicate that the  $\epsilon'$  decomposition product may be gradually approaching the composition of  $\epsilon$ -carbide.

A further problem which arises with the interpretation of these X-ray diffraction data concerns the question of martensite. The strongest X-ray reflection recorded for samples heated to  $205^{\circ}$  C has a *d*-spacing which corresponds to that of the first martensite doublet, but a doublet itself could only be resolved in samples heated to  $420^{\circ}$  C. Indeed, there is considerable confusion in the vicinity of this reflection, for the strongest  $\epsilon$ -phase line (and  $\epsilon'$  line) occur here also.



Figure 4 Differential thermogram obtained upon heating the splat-cooled alloy. Temperature difference  $\Delta T$  (arbitrary scale) plotted against temperature.

The X-ray diffraction results obtained for samples heated to 560° C revealed the existence of only ferrite and cementite, in agreement with Ruhl and Cohen's observation that these are the final decomposition products. However, in the present work it is apparent that the second differential thermal analysis (DTA) decomposition peak is associated not only with the growth of these two phases from the  $\epsilon$ -phase decomposition product, but also with the disappearance of austenite. Since the amount of austenite present is not very large, however, it is unlikely that the second DTA peak is due to austenite decomposition alone. Intuitively one would not expect much heat evolution from the second reaction which Ruhl and Cohen envisaged either, namely, the decomposition of martensite and  $\epsilon$ -carbide into ferrite and cementite. Indeed, no DTA peaks, other than those corresponding to austenite disappearance, have been observed in any other splat-cooled ferrous alloys or samples of water-quenched

TABLE III Lattice parameters and c/a ratios for the  $\epsilon$ - and  $\epsilon'$ -phases of Table I

Treatment	Phase	a(Å)	c(Å)	c/a	
Splat-cooled	e	2.629	4.323	1.644	
Heated to 205° C	$\epsilon'$	2.647	4.291	1.621	
Heated to 420° C	$\epsilon'$	2.642	4.317	1.634	
Reference [15]	e-carbide	2.754	4.349	1.576	



Figure 5 Transmission electron micrographs of electropolished foils after heat treatment: (a) aged 1 h at 200° C; (b) aged 1.5 h at 400° C.

filings [9, 11, 12], where a similar reaction to Ruhl and Cohen's second one would have occurred in the early stages of ageing. Admittedly, the relative amounts of martensite and  $\epsilon$ -carbide would probably be different in the Fe-Si-C alloy, owing to its higher carbon content, but it does appear more logical to associate the second peak with the transformation of the intermediate  $\epsilon'$ into ferrite and cementite. However, until the nature of the  $\epsilon$ -phase decomposition product can be established with more certainty, interpretation of the differential thermogram (Fig. 4) will remain speculative.

# 3.2.2. Metallographic examination

A brief metallographic study was made of the decomposition of the  $\epsilon$ -phase. Splats aged for 1 h at 200° C contained a h cp phase in electrontransparent areas, whose *d*-spacings were very close to those of the  $\epsilon$ -phase. Fig. 5a shows the microstructure observed after this heat treatment. The local contrast conditions determined whether the grains exhibited the "herring-bone" type of structure evident in the right-hand grain of the micrograph. In this particular case, tilting of the foil made this modulated pattern disappear from the right-hand grain and appear in the left-hand one. A specimen aged for 1.5 h at 400° C (Fig. 5b) showed a similar type of structure and the matrix remained h cp.

# 4. Discussion

# 4.1. The nature of the $\epsilon$ -phase

The observation of the hcp  $\epsilon$ -phase in two Fe-Ti-C alloys [9] and the Fe-Si-C alloy needs to be examined with a view to establishing whether this phase solidifies directly from the melt or whether it is a transformation product of austenite analogous to  $\epsilon$ -martensite. It is well known that an hcp phase in iron-base systems is stabilized by either pressure [10, 16] or certain alloying additions [17-19]. The alloy-stabilized hcp phase forms from austenite by a martensite reaction, which is greatly enhanced as a result of plastic deformation [20]. The principal effect of the alloying additions which are known to enhance  $\epsilon$ martensite formation is to reduce the stackingfault energy of the austenite, so that the small ribbons of hcp material which comprise stacking faults can act as nuclei for much larger regions of the hcp phase. Therefore, if the alloying elements in the Fe-Si-C and Fe-Ti-C alloys do lower the stacking-fault energy of austenite, the formation of large areas of hcp material will be favoured.

Quantitative determinations of the effect of silicon, titanium and carbon on stacking-fault energy have been made in Ni-Cr austenites, by measuring the radii of dissociated dislocation nodes. Silicon has been shown to produce a very marked reductions in stacking-fault energy in amounts up to 3.66 wt% [21, 22], which is consistent with Ruhl and Cohen's [2] observation that the percentage of  $\epsilon$ -phase increases dramatically with silicon content. Similar, though not so dramatic, reductions have been measured for titanium additions [23, 24]. Carbon, however, has an opposing effect. Studies [25, 26] on manganese and carbon steels have shown that carbon raises the stacking-fault energy of austenite up to carbon concentrations of 1.35%. This conflicts

directly with the contention [8] that  $\epsilon$ -phase forms because of the reduced stacking-fault energy of carbon-enriched austenite. It is nevertheless true that considerable amounts of carbon alone do promote  $\epsilon$ -phase formation [2] and thus there may be additional factors which influence stackingfault energy. For example, no measurements have been reported of the effect of carbon at higher concentrations, and no consideration has been given to possible interactions between different solute species and the effect such interactions may have on stacking-fault energy. Therefore, on the basis of stacking-fault energy considerations alone, it is not possible to decide whether  $\epsilon$ -phase is produced from pre-existing austenite or whether it forms directly from the melt.

In the transformation of fcc austenite to hcp  $\epsilon$ -martensite in steels with low stacking-fault energies, electron diffraction analysis shows that the close-packed planes of the two crystal structures are parallel [27]. Since the transformation is a martensitic reaction involving no atomic diffusion, the interplanar spacings of the austenite (111) planes and  $\epsilon$ -martensite (00.2) planes are equal. If this same equality exists in the splatcooled Fe-Si-C and Fe-Ti-C alloys it supports the view that the  $\epsilon$ -phase does form from austenite. In the Fe-Si-C alloy the average d-spacing of the  $(00.2)_{\epsilon}$  planes was 2.156 ± 0.008 Å, whilst that of the  $(111)_{\gamma}$  planes was 2.096 ± 0.006 Å. However, the mean austenite lattice parameter,  $3.633 \pm$ 0.011 Å, implies that the austenite contains only 1.85 wt%C, according to the equation derived by Ruhl and Cohen [2] for the compositional dependence of the lattice parameter. Yet, even if the austenite were to contain the overall alloy carbon content in solid solution, the interplanar spacing of the (111) planes would be only 2.140 Å. which is outside the error range of the *d*-spacings of the  $(00.2)_{e}$  planes. An even larger difference exists between the two interplanar spacings in the Fe-Ti-C alloys, and therefore this evidence suggests that the  $\epsilon$ -phase does not form as a martensitic product of austenite transformation.

Recently, Ishida and Nishizawa [28] have used a thermodynamic analysis to study the fcc  $\rightarrow$  hcp martensitic transformation in a series of Fe-Mn-X ternary alloys, in order to evaluate the effect of alloying elements on the relative stability of  $\epsilon$ -iron compared with  $\alpha$ - and  $\gamma$ -irons. They defined the function:

$$\Delta G_X^{\gamma/\epsilon \, \mathrm{Fe}} = \Delta G_X^{\mathrm{fcc} \to \mathrm{hcp}} + \Delta \Omega_{\mathrm{Fe}X}^{\gamma \to \epsilon} \tag{1}$$

to represent the effect of alloying element X on the relative stability of  $\gamma$  and  $\epsilon$  at 500 K (227° C), where  $\Delta G_X^{\text{fcc} \rightarrow \text{hcp}}$  is the free energy difference between fcc and hcp structures of pure component X, and  $\Delta \Omega_{\mathrm{FeX}}^{\gamma \to \epsilon}$  is the difference in interaction parameter in the  $\gamma$ - and  $\epsilon$ -phases. Thus, if  $\Delta G_X^{\gamma/\epsilon \ Fe}$  is negative, the alloying element X will stabilize the  $\epsilon$ -phase rather than the  $\gamma$ -phase. It was found that  $\Delta G_X^{\gamma/\epsilon Fe}$  was positive for all twelve of the alloying elements considered (Al, Co, Cr, Cu, Mo, Nb, Ni, Si, Ti, V, W, C) and, therefore, that these elements stabilize the  $\gamma$ -phase rather than the  $\epsilon$ -phase near 500 K (227° C). However, silicon was found to have the smallest value of  $\Delta G_X^{\gamma \epsilon Fe}$ , and therefore it is the most likely  $\epsilon$ -stabilizing addition of all the elements considered. Notwithstanding this,  $\Delta G_X^{\gamma/\epsilon Fe}$  values for both titanium and carbon are among the largest positive values, and hence both these elements strongly stabilize the  $\gamma$ -phase in preference to the  $\epsilon$ -phase. It is worth noting that stacking-fault energies in Fe-Mn-X alloys calculated from the parameter  $\Delta G_X^{\text{fcc} \rightarrow \text{hcp}}$  showed that titanium had one of the strongest effects in raising the energy, in sharp contrast to the results [23, 24] mentioned earlier.

On balance, then, it must be concluded that the  $\epsilon$ -phase does form directly from the melt. The stacking-fault energy data are inconclusive, but the comparison of equivalent interplanar distances in the fcc and hcp structures suggests that  $\epsilon$ -phase does not form from austenite, and the thermodynamic stability parameter shows that, at 500 K (227° C) anyway, the alloying additions under consideration favour formation of austenite rather than  $\epsilon$ -phase.

# 4.2. The decomposition of $\epsilon$ -phase

The X-ray diffraction results from the splat-cooled Fe-1.9 wt% Si-4.2 wt%C alloy heated past the first DTA peak were difficult to interpret, although it seems certain that the reaction postulated by Ruhl and Cohen [2] and supported by Boswell and Chadwick [5], namely,

$$\epsilon$$
-phase  $\rightarrow \epsilon$ -carbide + martensite

does not occur. The persistence of an hcp matrix after the first peak, together with the appearance of modulated microstructures in the aged thin foils, suggests that decomposition of  $\epsilon$ -phase may occur by a spinodal reaction. The "classical" indication that a spinodal reaction may exist in a given alloy system is the presence of a miscibility gap in the phase equilibrium diagram [29]. This criterion naturally applies only when the decomposing phase is an equilibrium phase above the miscibility gap. However, it is possible to have a metastable miscibility gap which is wholly submerged under the equilibrium diagram, and whose existence will only be revealed by the appearance of a new metastable phase [29].

The existence of a spinodal reaction in a given system requires that the phases which form from the decomposition process are crystallographically similar to the original phase; in the simplest case they have the same crystal structure and differ only in composition. The X-ray work on the aged hcp  $\epsilon$ -phase shows that it decomposes into an hcp product, designated  $\epsilon'$ , which has different lattice parameters from the original  $\epsilon$ -phase. Because of the broadness of the diffraction lines this  $\epsilon'$  product could be two hcp phases differing only slightly in carbon content and hence lattice parameter: one becoming enriched in carbon and approaching the composition of  $\epsilon$ -carbide; the other becoming depleted in carbon and approaching the "composition" of  $\epsilon$ -iron. This contention is supported by the electron diffraction pattern corresponding to Fig. 5, in which only one set of hcp reflections was evident.

The very nature of the "periodic" microstructure in this figure may also be used to infer that spinodal decomposition is occuring. Kelly and Nicholson [30] suggested that the presence or absence of the distinctive modulated microstructure in alloys with a high volume fraction of precipitate provides the best method of deciding whether or not an alloy has undergone spinodal decomposition. Furthermore, no grain boundary precipitate or precipitate-free zones were observed in any of the aged foils, which is also a good indication that decomposition is spinodal [31].

Unfortunately this evidence does not prove that the e-phase decomposes spinodally, but simply shows that the experimental data are consistent with this phenomenon. Indeed, it has been stressed [32] that it is unwise to rely on morphological evidence alone when predicting the existence of spinodal decomposition. It is worth noting, however, that since the time constant for spinodal decomposition is extremely small, very fast cooling rates are required to inhibit spontaneous reaction during the quench [29]. Therefore, spinodal reactions which would otherwise go to completion during quenching may be suppressed by splatcooling, and the unstable phase so produced would decompose during subsequent ageing. The observation of similar types of modulated microstructure in splat-cooled Ag-Cu [33], nickel superalloy [34] and Fe-W [35] alloys shows that such a phase transformation mechanism is a feature of many splat-cooled alloy systems.

# 5. Conclusions

(1) Almost 100%  $\epsilon$ -phase is produced in a splatcooled Fe-1.9 wt% Si-4.2 wt%C alloy, the remainder of the matrix being composed of austenite and very small quantities of non-crystalline phases. The  $\epsilon$ -phase is highly faulted and twinned, and occasionally contains a fine dispersion of precipitate particles. Its lattice parameters varied from run to run, confirming that the  $\epsilon$ -phase has a variable composition. It apparently forms directly from the melt, for in neither Fe-Ti-C alloys nor the Fe-Si-C alloy can it be accounted for as the transformation product of a low stacking-fault energy austenite.

(2) The decomposition of  $\epsilon$ -phase during heating does not appear to occur by the two-stage process advanced by Ruhl and Cohen [2]. X-ray diffraction and metallographic evidence indicate that it may transform by spinodal decomposition, although the evidence is not conclusive enough to verify this.

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