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Modification of γ-(Fe, Cr)$_3$C pseudo-binary eutectic

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The γ-(Fe, Cr)$_3$C pseudo-binary eutectic alloy with K, Ce, Sb additives was unidirectionally solidified in a Brigdman-type unit. The quasi-regular, lamellar eutectic carbide was changed into rods and bent blades by the modifiers under well-controlled conditions. At very slow growth, partial modification was common. At growth rates corresponding to a slightly cellular interface, a fully modified structure could be obtained. The modification behaviour as a function of the modifying element, its concentration and the growth rate is described and discussed.

1. Introduction

The γ-(Fe, Cr)$_3$C pseudo-binary eutectic is the main structural component of white cast iron at low chromium levels. Its as-solidified morphology determines the mechanical properties, especially toughness, of white cast iron which is still a popular wear-resistant material. The typical bulk-solidified eutectic carbide forms are characterized as ledeburitic and plate-like [1]; however, various other forms are reported to arise between them. While the term "plate-like" is quite straightforward, the "ledeburitic" eutectic refers to the structure in which (Fe, Cr)$_3$C forms the matrix, with rods and short lamellae of the γ-phase distributed in it. A recent investigation has shown that the volume fraction of the γ-phase in the ledeburitic structure ranges from 28 to 35%, i.e. much lower than its average value in the whole sample [2]. It has long been observed that the ledeburitic structure is very brittle, and the fine plate-like eutectic gives an improved toughness [3]. Much effort has therefore been expended in an attempt to eliminate the ledeburitic structure and to refine the carbide phase. The methods include

(a) alloying, i.e. other elements are added to the alloy to change the crystal type of the carbide phase [4–7], and

(b) the addition of minor elements to the melt before solidifying in order to effect eutectic inoculation and/or modification [8, 9].

Both have been applied in bulk and unidirectional solidification processing. The alloying method essentially changes the material to another alloy system. Whilst inoculation can promote the nucleation of eutectic phases, modification changes the phase morphology as a result of the eutectic growth process. The latter has been proved to be a very effective way of modifying the faceted phases in two common non-faceted–faceted engineering alloy eutectic systems, i.e. Al–Si and Fe–C (graphite), which have volume fractions of the faceted phase equal to 12.8 and 7.5%, respectively. The γ-(Fe, Cr)$_3$C eutectic belongs to the non-faceted–faceted group system, with the volume fraction of the faceted phase higher than 50%. Systematic investigation of its modification behaviour has not been reported in the literature, although some experiments with addition of mischmetal to commercial white cast iron have been reported recently [9].

This investigation is focused on modifying the (Fe, Cr)$_3$C phase with the addition of various impurities (modifiers). The experiment was carried out using unidirectional solidification in order to get a better understanding of the growth mechanism and the modification behaviour.

2. Experimental procedure

The base alloy used for the unidirectional solidification, namely Fe–4.25 wt % C–4.0 wt % Cr corresponding to the nominal composition of the γ-(Fe, Cr)$_3$C pseudo-binary eutectic [10], was pre-cast into small bars in a vacuum furnace under argon protection. Iron (99.99%), chromium (99.99%) and graphite (99.999%) chips were induction-melted in a recrystallized alumina crucible, heated to about 1600 °C for 20 min and then cooled to 1400 °C. The modifier was put into the melt 2 min before casting. The melt was then cast into a steel mould coated with zirconia. The modifiers used in this investigation were

(a) antimony, added in the form of pure metal (99.999%),

(b) potassium, added in the form of KCl powder (99.9%), and

(c) cerium, pure metal (99.99%).

The cast bars were remelted and unidirectionally solidified in a vertical Bridgman-type unit, described in detail elsewhere [2]. The remelting temperature was 1360 °C. The temperature gradient (G) at the solid–liquid interface was controlled between 11 and 15 °C mm^{-1}. The samples were solidified upward at rates of 2 to 1440 mm h^{-1}. At the end of each run (usually after growing 70 mm) the sample was quenched into water, and the growing solid–liquid interface was delineated.

The total length of each sample was about 130 mm. A longitudinal section was made by electrical discharge machining (EDM) around the solid–liquid interface, and transverse sections were made 15 mm beneath the interface. The sectioned samples were mounted and polished for metallographic examinations.

3. Results and analysis

3.1. Unmodified structure

The growth behaviour of the γ-(Fe, Cr)$_3$C eutectic without the addition of a modifier has been described elsewhere [2]. It can be characterized in two forms: planar growth and cellular growth, which are controlled by the ratio of the temperature gradient G to the growth rate R. At very large G/R the sample solidified with a planar solid–liquid interface, yielding a quasi-regular, lamellar structure. At moderate or small G/R values it displayed a cellular growth pattern. In the central region of each cell, the eutectic grows parallel to the heat extraction direction (sample lowering direction), resulting in an irregular but plate-like carbide. In the outer edge of each cell, the eutectic grows laterally into the liquid groove, producing a ledeburitic structure. For a given value of G, as the growth rate is reduced to a critical value, the solid–liquid interface becomes planar, the ledeburitic structure in the outer ring of the cell disappears and the irregular plate-like carbide tends to appear as quasi-regular lamellae. This tendency is illustrated in Fig. 1. The ledeburitic structure is denoted by the arrows in Fig 1(a), (b).

3.2. Potassium-modified structure

After modification with 0.2 wt % potassium (0.38 wt % KCl), the sample still displayed cellular

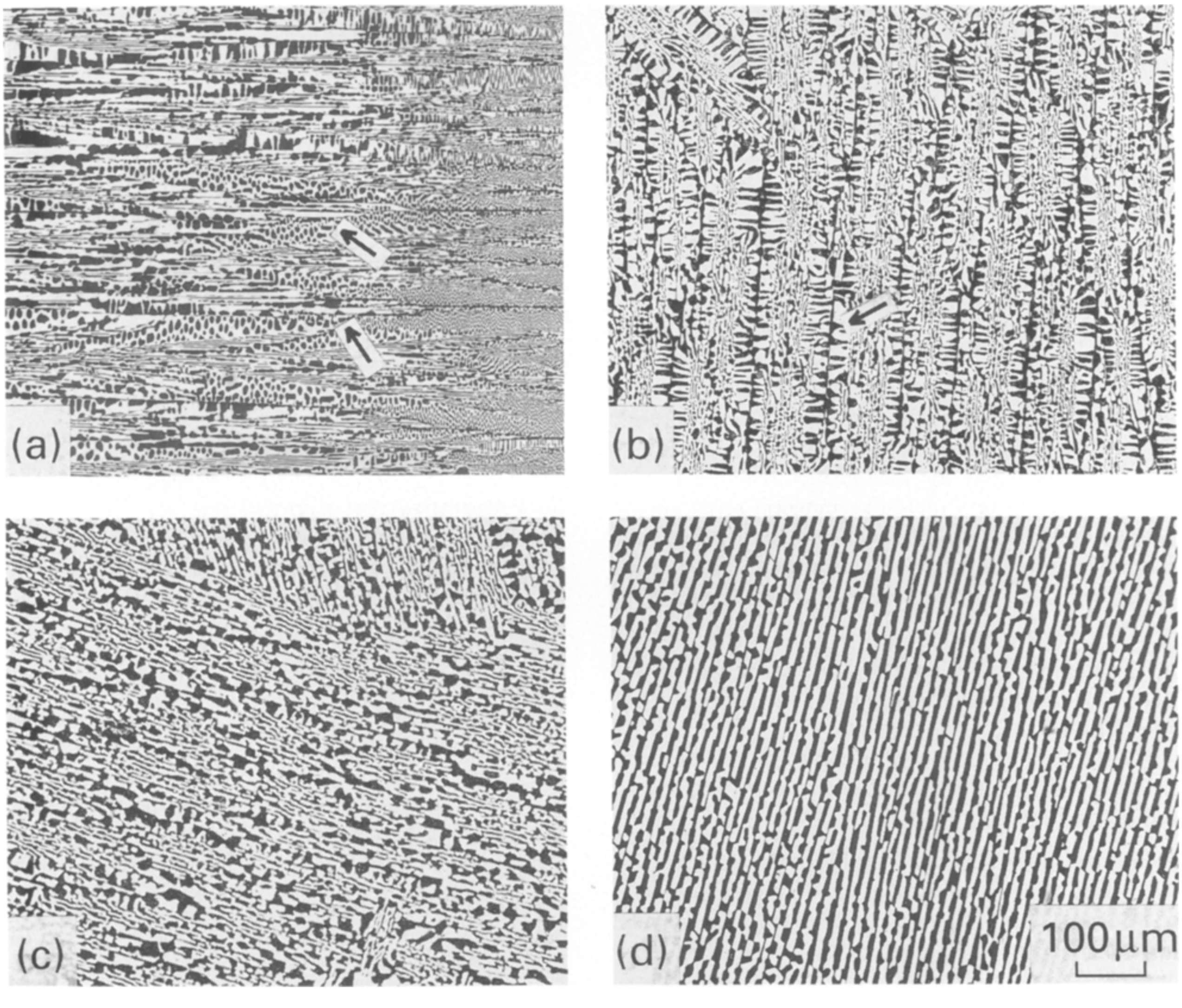

Figure 1 Unidirectionally solidified γ-(Fe, Cr)$_3$C eutectic without modifier. The white phase is carbide, the black phase is martensite transformed from γ-phase during quenching. (a) Longitudinal section, (b–d) transverse sections: (a) fast cellular growth, $R = 47$ mm h^{-1}, $G = 13$ °C mm^{-1}; (b) transverse section from the same sample as (a); (c) slightly cellular growth, $R = 13$ mm h^{-1}, $G = 14.6$ °C mm^{-1}; (d) planar growth, $R = 6$ mm h^{-1}, $G = 14.6$ °C mm^{-1}.

growth at small or moderate G/R values and planar growth at large G/R values. This is essentially similar to that of the unmodified samples. During cellular growth, the modified sample displays a stronger tendency for the irregular lamellae to split into rods in the central region of each cell. The ledeburitic structure resulting from lateral growth is still very evident, as shown in Fig. 2.

During planar growth, lamellar carbide has a strong tendency to split into rods and/or bent blades, as shown in Fig. 3. Most of the rods do not display a sharp faceted shape, while some of them have a rectangular shape in transverse section. The bent blades exhibit a more rounded, less faceted outline.

It is interesting to note that, while the eutectic structure in some regions is modified, other regions still remain as quasi-regular lamellae. This phenomenon is called "partial modification". The modified region usually occupies whole grains, i.e. some grains are modified while others are not. At a growth rate of 6 mm h^{-1} and with a 0.2% potassium addition, the modified structure occupies 40–50% of the whole area in the transverse sections. The percentage of the modified area can be raised by increasing the amount of potassium addition, but the increment of the modification effect is very limited. 0.525% potassium (1% KCl) could only give an approximately 55–60% modified area. Further additions did not show an increasing modification effect if the growth rate was very small.

For a given potassium addition, the modified area is increased as the growth rate is raised within the planar growth range. At the critical growth rate where the planar solid–liquid interface tends to become cellular, the sample is usually fully modified, i.e. the lamellar eutectic is replaced by rod-like or bent blade-like structure as shown in Fig. 4.

3.3. Cerium-modified structure

Fig. 5 shows the typical eutectic structure with 0.4% cerium. It can be seen that the carbide becomes rods, short lamellae and bent blades in the modified area. This structure is similar to that reported by Liang and Su [9] in a commercial white cast iron modified by mischmetal. Compared with those modified with potassium, the Ce-modified carbide rods have slightly stronger faceting tendency.

Partial modification is also common for the samples with cerium addition. The variations of modified area with the amount of modifier and the growth rate are similar to those observed in potassium-modified samples. Fig. 6 is a plot of the percentage of modified area against the growth rate with a 0.6% cerium addition. It can be seen that within the planar growth range, for

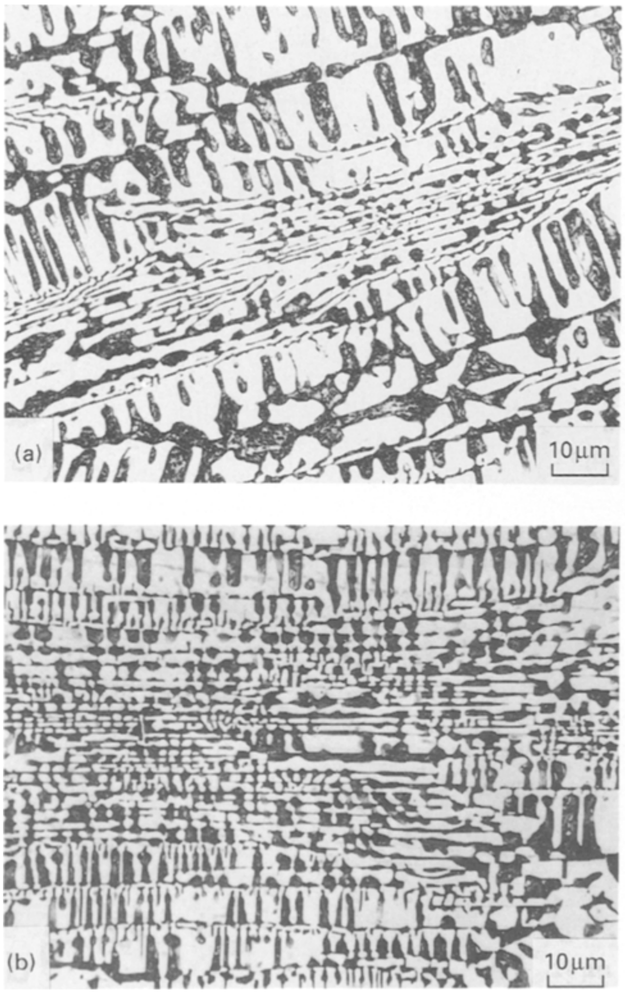

Figure 2 Eutectic structure with fast growth. $R = 1000\ \mathrm{mm\,h^{-1}}$, $G = 11\ ^{\circ}\mathrm{C\,mm^{-1}}$, transverse section: (a) pure alloy without modifier, (b) modified by 0.2 wt % K.

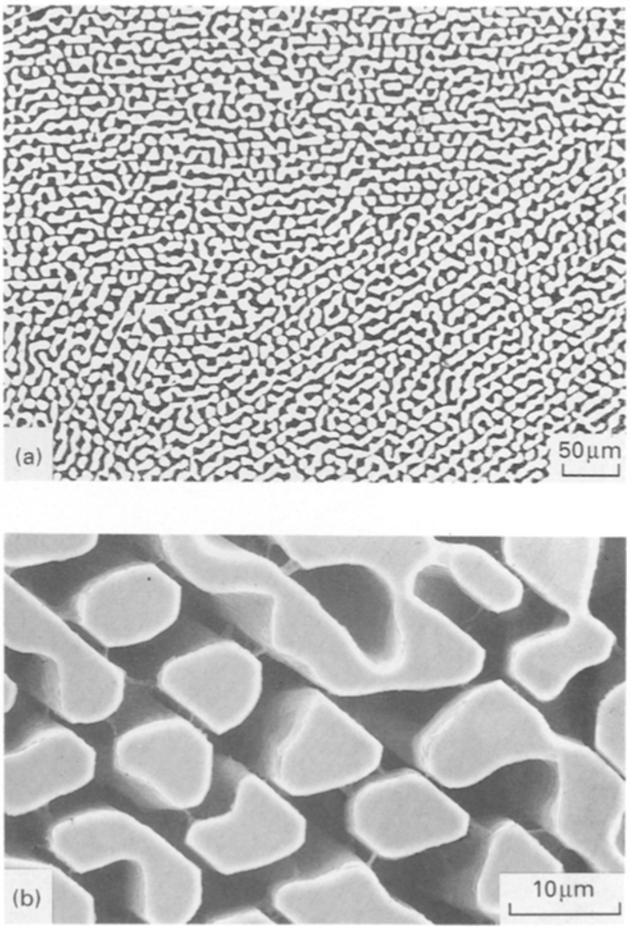

Figure 3 K-modified eutectic structure with planar growth. 0.2 wt % K, $R = 6\ \mathrm{mm\,h^{-1}}$, $G = 14.6\ ^{\circ}\mathrm{C\,mm^{-1}}$, transverse section: (a) optical micro-photography, (b) SEM photography.

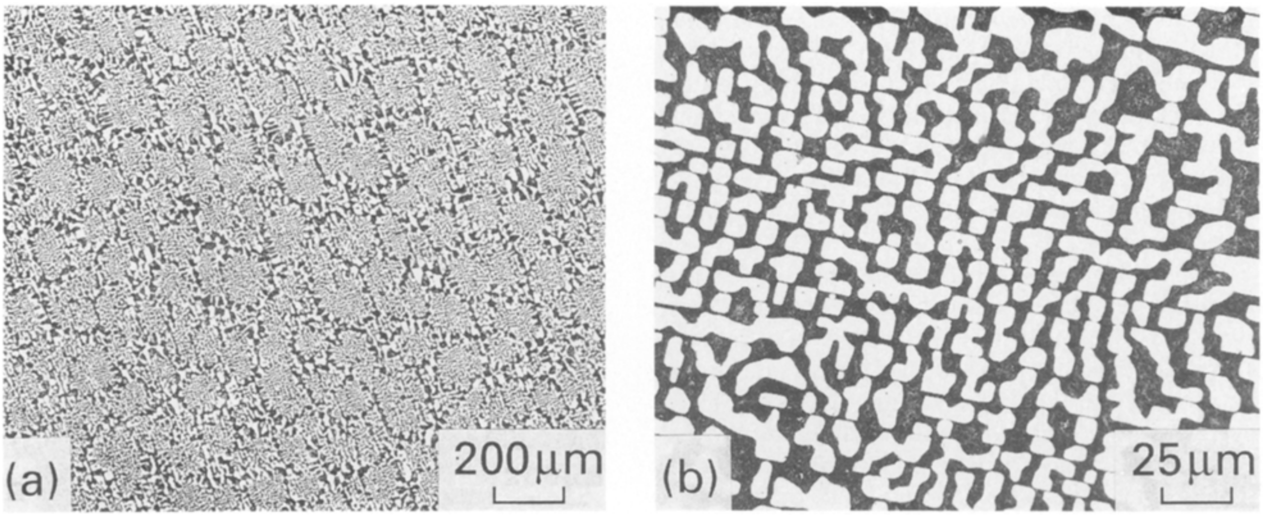

Figure 4 (a, b) Fully modified structure with slightly cellular growth. 0.2 wt % K, $R = 10\ \mathrm{mm\,h^{-1}}$, $G = 14.6\ ^\circ\mathrm{C\,mm^{-1}}$, transverse section.

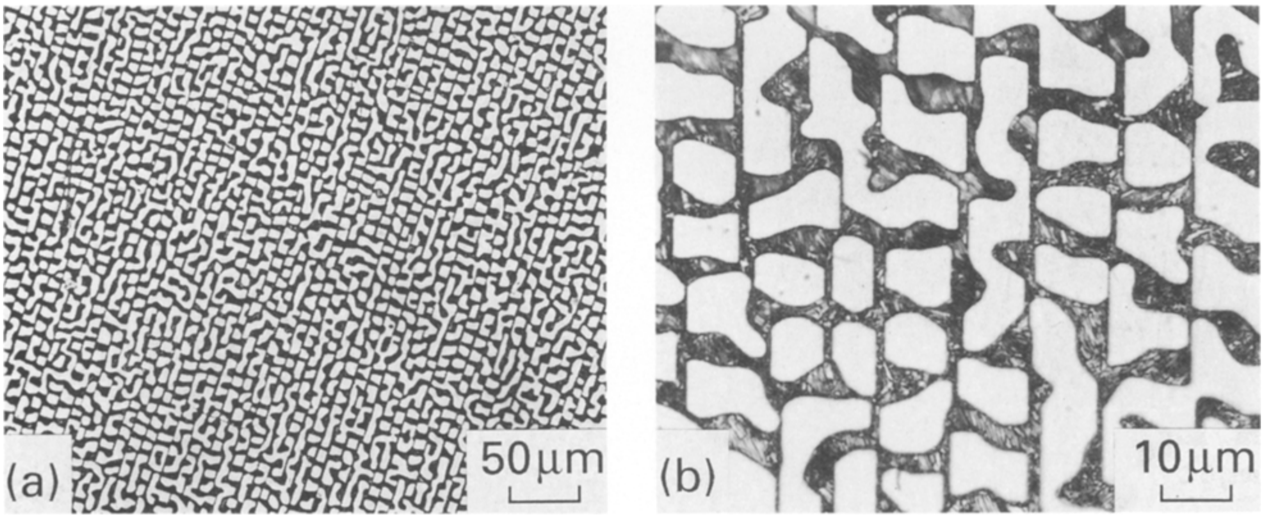

Figure 5 (a, b) Ce-modified eutectic structure with planar growth. 0.4 wt % Ce, $R = 6\ \mathrm{mm\,h^{-1}}$, $G = 14.6\ ^\circ\mathrm{C\,mm^{-1}}$, transverse section.

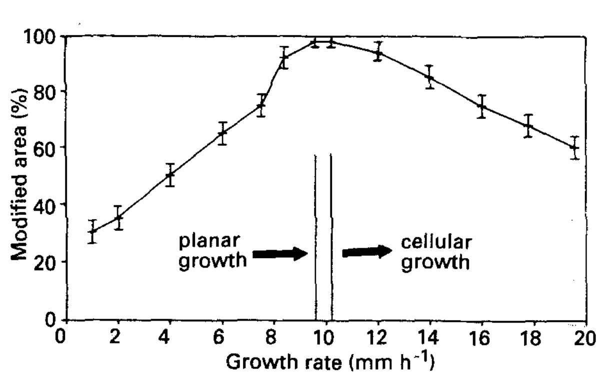

Figure 6 Relation between modified area and growth rate. 0.6 wt % Ce addition, $G = 14.6\ ^\circ\mathrm{C\,mm^{-1}}$.

a given cerium addition, the modified area increases with the growth rate. The sample becomes fully modified when the growth rate reaches the value where a transition from planar to cellular growth occurs. During cellular growth, more and more of the ledeburitic structure appears as the growth rate increases further, and thus the "modified" area decreases.

3.4. Antimony-modified structure

Fig. 7 shows the antimony-modified structure obtained during planar growth. Rod-like carbide is the predominant form in the modified area. The rods exhibit a marked faceted outline, having an approximately rectangular transverse section. Partial modification is also observed in the samples with antimony additions. However, as the amount of antimony increases, the unmodified area can be reduced to a small amount, e.g. a 1.4 wt % Sb addition can produce a sample with a 90% rod-like structure at a growth rate of $6\ \mathrm{mm\,h^{-1}}$ ($G = 14.6\ ^\circ\mathrm{C\,mm^{-1}}$, planar growth).

The residual antimony content in unidirectionally solidified samples was analysed by energy-dispersive spectroscopy (EDS) and wavelength-dispersive spectroscopy (WDS). In each sample, five measurements were made behind the solid–liquid interface. Each measurement covered 100 μm × 100 μm area. A mean value of five measurements was taken to define the residual antimony content. A plot of the modified area percentage versus the residual antimony content is shown in Fig. 8. The data in this plot are from samples solidified at a rate of 6 mm h^{-1}. It is seen clearly that, under given growth conditions, the modified area increases more rapidly with the residual antimony content at lower antimony levels.

It was found that the interphase spacing was not altered by the addition of a modifier, i.e. whereas the quasi-lamellar array for growth with a planar interface was replaced by a more rod-like form of carbide phase, the inter-rod spacing was closely similar to that of the quasi-lamellar phase likely to be present in the absence of the modifier.

3.5. Distribution of modifiers

The distribution of the modifier elements in the solidified samples was detected by EDS and WDS. The average concentration in the eutectic structure was obtained by scanning over a 100 µm × 100 µm area. The concentration in each phase was measured by point analysis.

Fig. 9 is the antimony concentration near the solid–liquid interface of a sample with a 1.0 wt % antimony addition, solidified at a rate of 8 mm h^{-1}. Two features can be clearly seen:

(a) there exists an accumulation of antimony in front of the solid–liquid interface during growth, and

(b) the distribution of antimony in the liquid phase in front of the interface follows the profile of the diffusion-controlled process.

In the two eutectic phases behind the solid–liquid interface, point analysis showed that the antimony exists mainly in the iron-rich phase. There is very little antimony in the carbide.

Samples with potassium or cerium additions were analysed with a method similar to that for antimony, but neither of them were detected. This may be due to the fact that the residual content of potassium and cerium is below the sensitivity level of the WDS employed (approximately 200 p.p.m.).

4. Discussion

The modification behaviour of γ-(Fe, Cr)$_3$C eutectic with the modifiers described herein can be characterized by saying that, when present, (a) the lamellar carbide splits into rods and (b) the modified carbide phase exhibits a weak faceting tendency.

Compared with the two eutectic phases, all of the modifiers applied in this investigation have low melting points. According to the Fe–Sb, Fe–Ce, Fe–K phase diagrams [11], all of them have very low partition coefficients in the iron phase. WDS analysis has shown that antimony has an even lower partition coefficient in the carbide phase than in the iron-rich phase. The situation may be the same for potassium and cerium. Since the partition coefficients of the modifying elements are small in both phases, then it is to be expected that these elements will be accumulated ahead of any advancing solid–liquid interface. Where the interface is macroscopically planar, as in pseudo-lamellar growth, then the concentration of the modifying element will vary from place to place, being

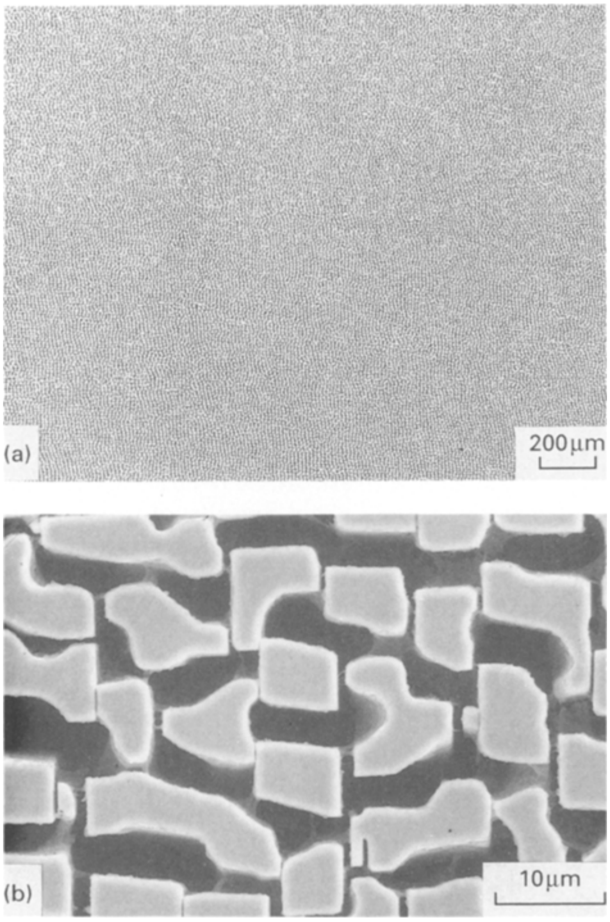

Figure 7 (a, b) Sb-modified eutectic structure in planar growth. 0.6 wt % Sb, R = 6 mm h^{-1}, G = 14.6 °C mm^{-1}, transverse section.

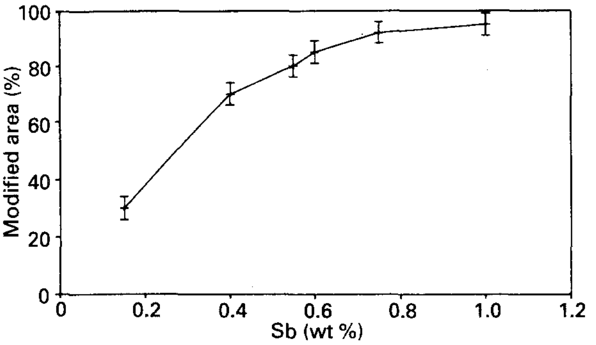

Figure 8 Relation between modified area and Sb content. R = 6 mm h^{-1}, G = 14.6 °C mm^{-1}, planar growth.

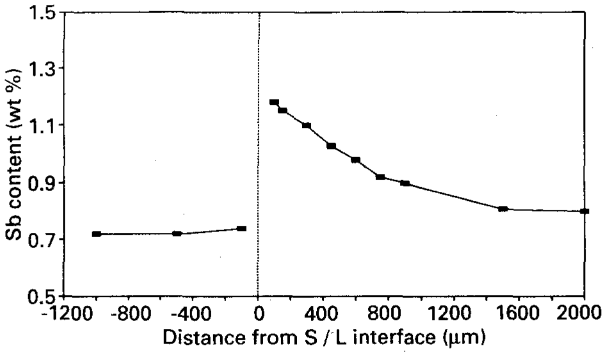

Figure 9 Distribution of Sb near a solid–liquid interface. 1.0 wt % Sb addition, R = 8 mm h^{-1}, G = 14.6 °C mm^{-1}.

greatest ahead of the centre of each carbide lamella. A high concentration of a low melting-point solute will reduce the local solid–liquid equilibrium temperature, and so retard the growth of the carbide phase. If the carbide phase as presented to the liquid is broad, then the local solid–liquid interface will be concave. Should the temperature gradient be small then the adjoining γ-phase will branch to occupy the "dent" as the sample solidifies. During this process, the concaved carbide has at least two choices for development: (a) splitting into two thinner lamellae along the central line of the original lamella, and (b) splitting into rods. It seems that the choice (a) should be preferred in terms of shortening the lateral diffusion distance of the solute. In such a case the lamellar spacing will be reduced to a half of its original value. However, this will not be favoured by the organization of the whole system with a given composition and growth rate. The system will eventually select (b), which can shorten the lateral diffusion distance without reducing the particle spacing significantly. After splitting, the rods would display a rectangular (instead of square) cross-section.

It was proposed by Liang and Su [9] that the γ-(Fe, Cr)$_3$C eutectic was modified by mischmetal through a mechanism of changing the leading phase from carbide to γ-phase. They found that γ-phase led as the mischmetal addition was increased. It was observed in the present investigation that the selection of the leading phase was mainly controlled by the carbon content of the base alloy, although a retardation effect of the modifier on the carbide phase was expected. An alloy with slight hypo-eutectic composition would solidify with the γ-phase leading during planar growth. Its ability to lead should disappear as the carbon content of the alloy is increased. At eutectic or slight hyper-eutectic composition, carbide phase was seen to be leading. The splitting of the carbide was favoured when the γ-phase was leading in a sample with a slightly hypo-eutectic composition and modifier. However, it was found that a "pure" alloy, i.e. without modifier, would not be modified even if it was solidified with γ-phase leading. On the other hand, the modified structure could be obtained when the alloy composition was slightly hyper-eutectic with the carbide phase leading. This confirms the observation that the carbide splits following the dent-formation mechanism proposed here, while the leading-phase mechanism may apply for the hypo-eutectic alloy.

It is a common occurrence that, within the planar growth range, the modified area on a microsection is increased as the applied growth rate is raised. This may also be attributed to the solute effect caused by modifier accumulation in front of the solid–liquid interface. For a given solute content in the sample, the accumulation become more serious as the growth rate is increased. The enhanced accumulation would help the carbide phase to split into rods.

When the growth rate reaches the value at which the solid–liquid interface begins to transform from a planar to a cellular form, full modification can usually be obtained. In order words, slightly cellular growth seems to enhance splitting of the carbide phase. A mechanism proposed by Hunt and Chilton [12] for a non-faceted–non-faceted binary eutectic system may work at this stage. They demonstrated that the regular lamellar eutectic could transform into a rod-like structure when constrained to grow laterally, perpendicular to the interlamellae interface plane. For the current quasi-regular lamellar eutectic, slightly cellular growth together with modifier accumulation yields the fully modified structure.

Whilst the antimony-modified carbide mainly exhibits faceted rectangular rods, some carbide regions modified with potassium or cerium appear as bent blades without any apparent faceting tendency. This might be attributed to chemisorption. It is well accepted that the faceted shape of a crystal is a direct result of anisotropic growth [13]. This growth anisotropy of the faceted phase can be reduced when some foreign element atoms are chemically adsorbed on to certain crystal planes. The chemisorption mechanism has been proposed for several non-faceted–faceted eutectic systems, e.g. Al–Si [14–16], Sn–Bi [17], Bi–Cd and Bi–Au$_2$Bi [18]. Potassium is a well-known modifier for the silicon phase in the Al–Si eutectic. Cerium has also been used to modify the graphite phase in the Fe–C eutectic [19]. All of their modification effects are supposed to work through a chemisorption mechanism. The transition of the (Fe, Cr)$_3$C phase from a faceted to a non-faceted shape may also be rationalized in terms of the chemisorption of these elements.

Compared with antimony, potassium and cerium are more active. They are liable to be lost from the melt during any slow solidification process. Atomic absorption spectroscopy analysis of the quenched portion in front of the solid–liquid interface shows that the potassium and cerium contents in the liquid phase are much lower than that of antimony. This may be the reason whey some carbide regions in the samples modified with potassium or cerium do not split into rods but retain their bent blade-like shapes. The segregation of potassium or cerium in some regions may not reach a level high enough to promote the splitting of the carbide lamellae. However, by adsorption on to its surface they can make the carbide change its growth pattern, resulting in the bent, non-faceted blades.

Based on the quantity added into melt, the modification abilities of the modifiers used in this experiment can be listed in the following sequence.

(a) splitting carbide into rods: Sb > Ce > K,

(b) promoting the transition from faceting to non-faceting: K > Ce > Sb.

5. Conclusions

The following conclusions can be drawn from this investigation.

(a) The γ-(Fe, Cr)$_3$C pseudo-binary eutectic can be modified by impurity addition together with well-controlled unidirectional solidification conditions. During fast cellular growth the carbide can be refined by impurities, but the ledeburitic structure produced by lateral growth cannot be eliminated. A fibrous eutectic may be obtained during planar growth.

(b) Within the planar growth range, the modification effect becomes stronger as the growth rate increases for a given modifier addition. The best modification can be achieved at the growth rate corresponding to the transition from planar to cellular growth.

(c) Antimony modifies the $(Fe,Cr)_3C$ phase by depressing the interface temperature, resulting in a faceted rod-like structure, whilst potassium works through a chemisorption mechanism, mainly yielding non-faceted, bent blade-like carbides. Cerium displays some features of both mechanisms, but not as strongly as either of them, producing a mixture of the above two morphologies.

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