Suplemento de la Revista Latinoamericana de Metalurgia y Materiales 2009; **S1** (3): 1391-1400

SOLIDIFICATION AND LIQUID´S GRADIENTS III: PLATEAU/RAYLEIGH INSTABILITY AND MARANGONI FLOW IN THE BRANCHING OF EUTECTIC GRAPHITE OF FLAKE CAST IRON

Alicia Norma Roviglione

- ✓ Este artículo forma parte del "Volumen Suplemento" **S1** de *la Revista Latinoamericana de Metalurgia y Materiales* (*RLMM*). Los suplementos de la RLMM son números especiales de la revista dedicados a publicar memorias de congresos.
- ✓ Este suplemento constituye las memorias del congreso "*X Iberoamericano de Metalurgia y Materiales (X IBEROMET)*" celebrado en Cartagena, Colombia, del 13 al 17 de Octubre de 2008.
- ✓ La selección y arbitraje de los trabajos que aparecen en este suplemento fue responsabilidad del Comité Organizador del *X IBEROMET*, quien nombró una comisión *ad-hoc* para este fin (véase editorial de este suplemento).
- ✓ La *RLMM* no sometió estos artículos al proceso regular de arbitraje que utiliza la revista para los números regulares de la misma.
- ✓ Se recomendó el uso de las "Instrucciones para Autores" establecidas por la *RLMM* para la elaboración de los artículos. No obstante, la revisión principal del formato de los artículos que aparecen en este suplemento fue responsabilidad del Comité Organizador del *X IBEROMET*.

Suplemento de la Revista Latinoamericana de Metalurgia y Materiales 2009; **S1** (3): 1391-1400

SOLIDIFICATION AND LIQUID´S GRADIENTS III: PLATEAU/RAYLEIGH INSTABILITY AND MARANGONI FLOW IN THE BRANCHING OF EUTECTIC GRAPHITE OF FLAKE CAST IRON

Alicia Norma Roviglione

Departamento de Ingeniería Mecánica- Facultad de Ingeniería- Universidad de Buenos Aires

** E-mail: arovi@fi.uba.ar*

Trabajos presentados en el X CONGRESO IBEROAMERICANO DE METALURGIA Y MATERIALES IBEROMET
Cartagena de Indias (Colombia), 13 al 17 de Octubre de 2008

Selección de trabajos a cargo de los organizadores del evento

Publicado On-Line el 29-Jul-2009
Disponible en: *www.polimeros.labb.usb.ve/RLMM/home.html*

Abstract

In the present work experimental evidence was submitted on the growth mechanisms of graphite phase in flake cast iron. These would not be controlled by crystalline deffects, the graphite/liquid interface would be a high mobility one and able enough to fit his growth direction to the local driving force direction. Then, flake cast iron would be assigned to irregular nf-nf eutectic class. It is shown that the branching process take place in the wide dimensions of the flake instead of the thickness and must be treated with a three dimensional geometry. It is proposed that the onset of the branching is related to the appeareance of Plateu Rayleigh instabilities (driven by surface tension instead of solute pile up). It happens in the neigbourg γ at the the triple contact line (graphite/γ/liquid) level. The necessary existence of bidimensional surface tension gradients provoked by the segregation of surface active elements and the corresponding conjugate flow of matter (Marangoni flow) was stated. The treatment procceds trough a metaphor with wide know surface tension assisted spreading and trough a heuristic analogy guided intuiton permits quick understandig of the fenomenon .

Keywords*: Flake cast iron, irregular eutectic spacing, Plateu - Rayleigh instability, Marangoni flow.*

Resumen

El presente trabajo ofrece evidencia experimental acerca del mecanismo de crecimiento del grafito en las variedades laminares de la fundición. Éste, no sería controlado por defectos, cristalinos, y la interfaz grafito/líquido sería de alta movilidad y elevada capacidad para adaptar su dirección de crecimiento a la dirección local de la fuerza impulsora. Por lo cual, debería asignársele la categoría de eutéctico irregular nf-nf. Se muestra como el proceso de ramificación del grafito procede en el ancho de la lámina y no en el espesor debiendo tratárselo dentro de una geometría tridimensional. Propone que el inicio de la ramificación está relacionada por la aparición de inestabilidades del tipo de Plateu/Raleigh (dinamizadas por la tensión interfacial y no por apilamientos de solutos) que ocurren en la fase vecina γ a nivel de la línea de triple contacto (grafito/γ/liquido). Establece la necesaria existencia de gradientes bidimensionales de tensión interfacial provocados por segregación de solutos superficialmente activos y de los respectivos flujos conjugados de materia (flujos de Marangoni). El tratamiento procede mediante una metáfora con fenómenos de mojado dinamizados por gradientes de tensión interfacial ampliamente conocidos y produce, mediante una intuición asistida ó guiada por la analogía heurística una comprensión inmediata del fenómeno.

Palabras Claves: *Fundición gris laminar, espaciado eutéctico irregular ,Inestabilidad de Plateu - Rayleigh; Flujos de Marangoni.*

1. INTRODUCTION

Very fine microstructure consisting of a two-phase solid dispersion is currently obtained when a binary eutectic alloy solidifies. This microstructure is approximately ten times finer than cells or dendrites formed under the same condition. So, an extremely large solid-solid interface by unit volume ratio exists. The exact arrangement of the two phases was determined by the intrinsic nature of the particular eutectic pair and solidification conditions. A relationship between eutectic morphology and fusion entropies of components seems to exist. On that basis, and on the consequent solid-liquid interface kinetics adopted by the components during eutectic growth, Hunt and Jackson [1] proposed a simple classification for the main types of observed

0255-6952 ©2009 Universidad Simón Bolívar (Venezuela)

morphologies. They would be 1) non-faceted/ non-faceted eutectics (nf-nf), 2) non-faceted/ faceted eutectics (nf-f), and 3) faceted/ faceted eutectics (f-f). Low fusion entropy components would exhibit a non-faceted solid-liquid growing interface. If a eutectic consists of a pair of these nf components, a nearly isotropic diffusion controlled growing kinetics takes place. It proceeds under low undercooling and the resulting morphology looks quite regular. Otherwise in nf-f and f-f eutectics one and two high entropy of fusion component are present, respectively. These f components would display a highly non-isotropic defect controlled lateral growth kinetics [2] and the resulting morphology would be quite irregular.

The modeling of nf-f eutectics is very important. Gray cast iron, an ancient material widely used up to day, belongs to this class. It participates of the three main features of nf-f irregular eutectic growth summarized by Fisher and Kurz [3] and Kurz and Fisher [4].

If we compare nf-f whit nf-nf eutectics the following characteristics can be noted

1) The degree of structural regularity is much lower and a wide dispersion of local spacing between both phases is observed.
2) For a given growth rate and fraction of phases, the average spacing and the supercooling for growth of a nf-f eutectic is much larger than for nf-nf eutectics.
3) For a given growth rate, the supercooling and the spacing decrease as the imposed temperature gradient increases. No such effect is seen for nf-nf eutectics.

As early hypothesis, based on that attachment difficulty of the atoms to the faceted interface will provokes additional contribution to supercooling (called "kinetic" supercooling), was shown experimentally that have not real foundation [5,6]; a new hypothesis was suggested: "... the large supercooling were due to the difficulties of adjusting the spacing to minimize the diffusion distance. *These difficulties are related to the anisotropy of growth of the faceted phase"* [6 as quoted by 7]. (The bold type comes from the present author).

Fisher and Kurz [4] made measurements of spacing and supercooling on camphor-naphthalene system (this system may growth in two distinct eutectic growth forms, one regular and the other irregular). They observed that, at a given growth rate, the spacing between phases (characterized by λ_E) selected by the eutectic growing in the irregular mode, are much larger than the similar one in the regular form. But, indeed, both values: $\lambda_{E\ irregular}$ and $\lambda_{E\ regular}$, lie on the same theoretical curve for the dependence of supercooling ΔT vs. λ_E derived for the regular form. So, they concluded that the coarseness of the structure is responsible of the large supercooling.

Trying to explain the origin of the large spacing, Fisher y Kurz [8], Magnin and Kurz [9], Magnin and Trivedi [10] and Magnin et al [11]; focussed their attention on the mechanism that controls, for irregular eutectic an at a given velocity, the stable growth range spacing (between a λ_{Emax} and $\lambda_{Emin)}$. Underlying all these approach there is a *basic hypothesis*: the f phase exhibits an intrinsic stiffness that impedes changes in the growth direction necessaries to fulfill diffusion requirements. The stiffness would come from the defect controlled lateral growth kinetics of the faceted phase. So, lamella always grows following a particular and fixed crystallographic direction. According to this, lamellar irregular eutectic growth would proceed as follows:

The local spacing decreases between two converging lamellae and increases between diverging lamellae. For converging lamellae, when their separation decrease below the extremum value, one of the lamella is pinched off. For diverging lamella, when the local spacing increases beyond a critical value, Fisher and Kurz [8] have suggested that the faceted phase branching in two diverging lamellas. The formation of the new lamella decreases the local spacing. The anisotropic growth kinetics of the faceted phase leads to what is termed *branching limited growth***.** Several criterions have been proposed to determine the maximum value of the spacing where the branching takes place. In [8], [9] and [11] it is suggested that this branching instability occurs when the faceted phase interface develops a depression of a some characteristic depth; (e.g. when it drops below a line joining the two triple point for the lamella). The average spacing lies between the minimum spacing and the spacing that cause the branching instability. Magnin et al [11] argue that the mechanism that stabilizing the minimum and maximum spacing **remains undetermined.** (The bold type comes from the present author).

If the precedent description were correct, under constrained growth experiments, we would predict that the crystalline growth direction of the faceted phase would exhibit oscillatory (zig-ag) changes related to the externally imposed growth direction.

In particular, in the cited work by Magnin and Kurz [9], they present a two-dimensional analytical model of irregular eutectic growth that participates of the previous discussed features and apply to the Fe-C system. They claim a good agreement between theoretical model and own experimental evidence previously published. But, more recently, Roviglione and Hermida [12], using an X-ray diffraction method and special sample preparation [13] have been able to determined growth direction relationship between austenite and graphite in type A flake cast iron directionally growth. They found that zigzag oscillatory change in growth direction of graphite does not exist. On the contrary, a strong relationship between graphite and austenite growth direction and external imposed growth direction was determined, it was:

Predominantly $\mathbf{<100>_{\gamma}}$ // $\mathbf{<11.0>_{Graphite}}$ // growth direction **(GD)**, followed by a significative proportion of $\mathbf{<10.0>_{Graphite}}$ **// DC** and in a lesser extension $\mathbf{\{10.1\}_{Graphite}}$ $\perp$ **GD**. The two first components account for the 80% of grains of graphite phase.

Besides, microstructure of frozen solid liquid interfaces of flake cast iron samples (as was reported by several researches [14,15,16]) does not look like the model of branching limited growth model requires. *It does not matter if the quenched procedure was performed on restricted or free growth solidification experiments*:

1. At the solid/ liquid front Graphite is always the leading phase, sometimes quite ahead from austenite.
2. The lamella frequently exhibits a wavy aspect, with not facets and always has a sharp extremity that looks as a point in a two-dimensional section.
3. Depression on the minor dimension of the lamella was never documented.
4. At the triple contact line (TCL) the contact angle (θ) between austenite and graphite correspond to wetting condition ($\pi/2 \geq \theta$) (otherwise the model propose $\pi \geq \theta \geq \pi/2$).

Finally, arguments based on that graphite phase always grows with a defect controlled lateral growth kinetics must be revised, specially because there exists evidence of a transition to uniform diffusion controlled growth when some elements of the IV group (like S or O) are present in the melt [17].

On the basis of the preceding statements, a search for the mechanism that controls the branching of minor phase in cast iron irregular eutectic was performed. New experimental evidence were obtained from scanning electron microscopy (SEM) observation made on samples of Ni alloyed gray cast iron directional growth with a new technique [18]. The microstructure of frozen solid liquid interface was retained by quenching [19] and revealed by chemical deep etching technique. Branching mode of the minor phase was observed, it occurs in the longer dimension of the flake.

A qualitative tri-dimensional model for branching controlling mechanism is proposed. In that model the interfacial tension plays a major role. Gradients of interface tension associated with thermal and solute profiles existing at the interface would drive fingering of austenite. This model was heuristically derived from similar fingering phenomenon observed when fluids with two components (one of them volatile) wet a solid substrate in the presence of thermal gradients.

2. EXPERIMENTAL PROCEDURE

Ingot 3 mm of diameter of cast iron was constrained growth at 1,2 μ/seg rate with an imposed thermal gradient of 393K/cm in front of the solid liquid interface. The composition of the melt is given in table 1.

Tabla 1. Cast iron alloy composition

Elements	C	Si	Ni	P	S	Fe
% (w/w)	3.84	2.51	5.8	0,054	<0,035	balance

During directional solidification of type A flake cast iron, a quenching procedure described elsewhere [18] was performed.
The ingots were cut in a plane containing the axis an submitted to the usual polishing sequence of silicon carbide paper up to 600 mesh and diamond paste up to 1μ.

Ferrite, a component of the matrix that generally surrounds the graphite phase, was selectively

removed by severe deep etching with 20% nitric acid solution in ethanol. The samples were immersed on the cold solution and gently agitate for few minutes (4-5).

Optical microscopy and SEM exploration at successive high magnification of selected zone of the quenched solid liquid interfaces was done.

3. RESULTS

Fig. 1 is a low magnification SEM micrography of a frozen solid/liquid interface of type A flake cast iron directionally grown. It was taken after deep etching. As can be seen, the growth of the majority of the flakes has been interrupted. But, in a few zones at the interface, copious branching of some isolated flakes can be appreciated.

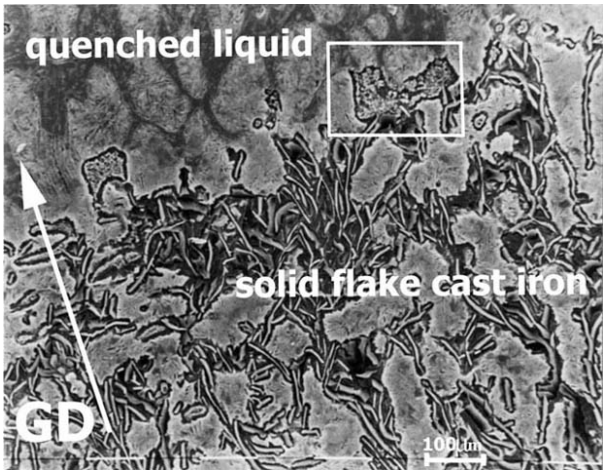


Figura 1. Frozen solid/liquid interface of type A flake cast iron directionally grown. SEM (low magnification).

Fig. 2 is a magnification of marked zone of Fig.1.

Fig. 3 shows graphite branching at more high magnification, many features can be remarked: 1) the “daughter” flakes evolves with continuity from the mother flake. That is, we are looking a branching process, not a re-nucleation of independent very fine flakes; 2) the daughter flakes are located along the major dimension of the mother flake and; 3) they are twisted out of the plane of the mother flake on a big angle.



Figura 2. Magnification of marked zone of Fig.1.SEM

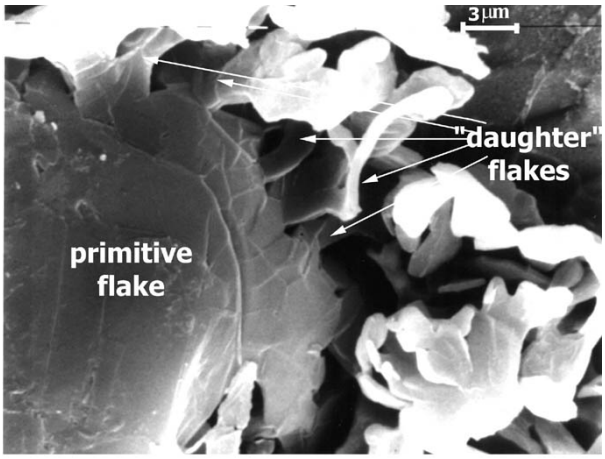


Figura 3. Branching mode of a singular primitive flake.

Fig. 4 is another view of “daughter” flakes, again some periodicity can be observed in the spacing between them, and also some “cuts” (indicated by arrows in the micrography) can be seen.

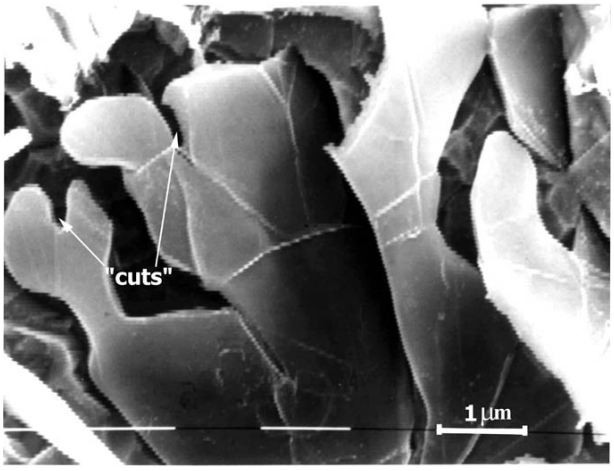


Figura 4. Periodic spacing of “daughter” flakes.

Finally Fig.5 a) and b) are optical micrographies, 50X and 150X respectively, obtained from another quenched sample.



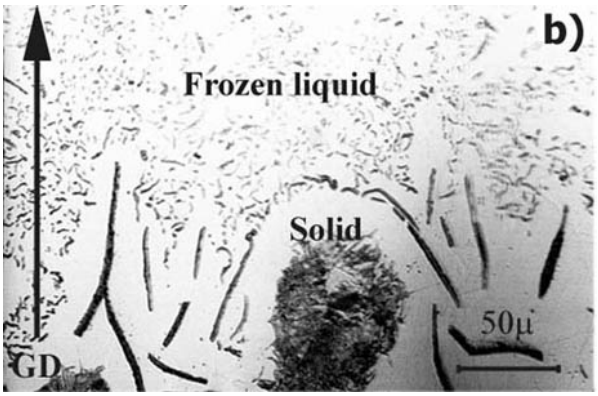


Figura 5 a) and b). Optical micrographies of a frozen interface. 50X and 150X respectively. 2% nital etched.

Fig5 c) correspond to a SEM photograph of lightly etched zone of solid liquid interface showing it in details.

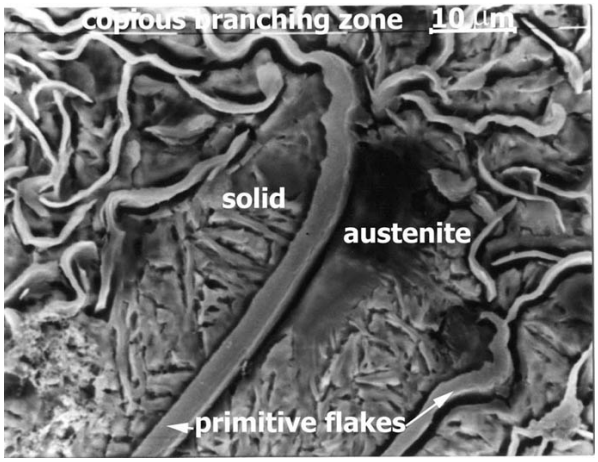


Figura 5 c) SEM photograph of lightly etched zone of this solid liquid interface showing more details.

As can be seen in this opportunity the quenching procedure was not so effective as in the previous occasion. Consequently, before the metastable eutectic lederburite had stopped the interface there was time for the branching process took place along of the entire interface. We observed, just in front of the primitive solid liquid interface, a zone with a lot of very fine flake graphite.

A further consideration seems to be appropriate: N*o evidence of facets on the growing interface, was observed*. Especially noticeable was the rounded end and smoothly curved appearance of the flakes and the wavy aspect of the flakes when they protrude into the zone where intense branching is observed Fig.5 c).

4. DISCUSION

All the branching process looks like if the following sequence had taken place: 1) a “scissors” makes small cuts, roughly equidistant, on the major dimension of the primitive flake, b) after that, each strip rotates out of the plane of the primitive flake and keeps on growing.

Early proposed mechanism of branching of graphite was sketched in the sequence of drawings Fig. 6 a), b) and c)[20]. The first drawing in Fig.6 a) represents direct “splitting” of the flake on the minor dimension, and would be in accord with the mechanism proposed in the “branching limited growth” model. But, there are opinions [21] in the sense that mechanism depicted in Fig.6 a) is only a misinterpretation of mechanism illustrated in Fig.6 b). Both pictures are inspired on observation made on Ni-C system eutectic. Only the latter picture, Fig.6 c), is a schematic representation of the branching mode proposed to illustrate the observed branching in commercial cast iron as quoted by Minkoff [22].

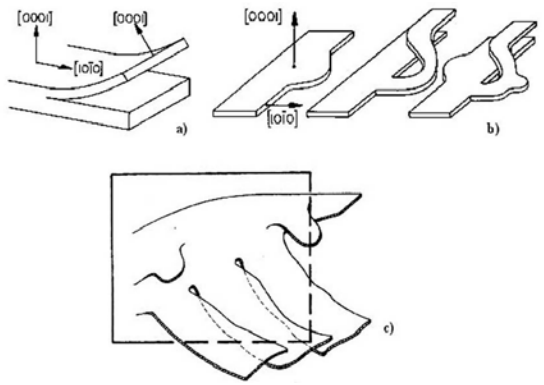


Figura.6: Proposed mechanism of branching: a) “splitting”; b) lateral branching an overgrowth; c) schematic of graphite branching observed in cast iron.

In the text the cited author writes:"...The graphite behavior is reminiscent of dendritic branching with no apparent cooperation involving the second phase". *In the case that this supposition was truth, it would be hard to explain reduction of the spacing whit increasing thermal gradient imposed as was observed.*

On the basis of the presented evidence and objections made on the current interpretation of the branching mode of graphite, seems to be necessary to explore an alternative explanation for the onset of the branching of graphite in flake cast iron irregular eutectic.

For the new proposal we will use:

1) Observation doing on our photographic evidence as Fig 5 a), b) and c), of the contact angle formed between austenite and graphite in frozen flake interfaces of Fe-C-Si-Ni system, and similar one reported by another researchers; see by example [14,15,16]).
2) An analogy whit fingering provoked by Marangoni stresses at the (TCL) as results of gradients of surface tension associated whit thermal gradients and solute profile [23].
3) Published data on surface tension of iron and its binary alloy [24] (giving special attention to the effect of S and O contents and on the thermal coefficient of surface tension).

First, we want to reproduce a nice photograph from Lux and Kurz [14]; Fig.7.

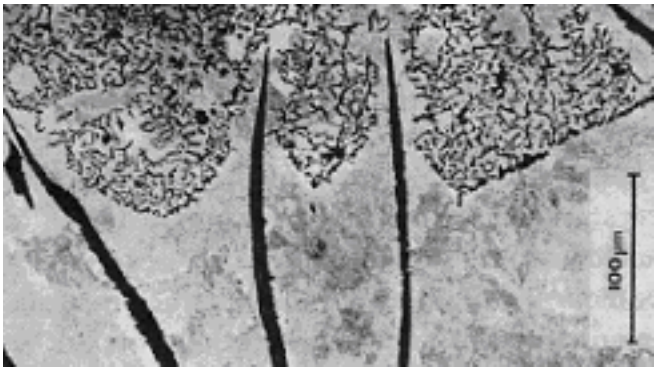


Figura 7. Frozen flake cast iron interface showing wetting of G by γ and γ valleys formed due to solute accumulation between flakes.

This is very representative of how Fe-C flake eutectic frozen solid liquid interface looks. It will be used to propose a tri-dimensional sketch for the interface as was depicted in Fig. 8.

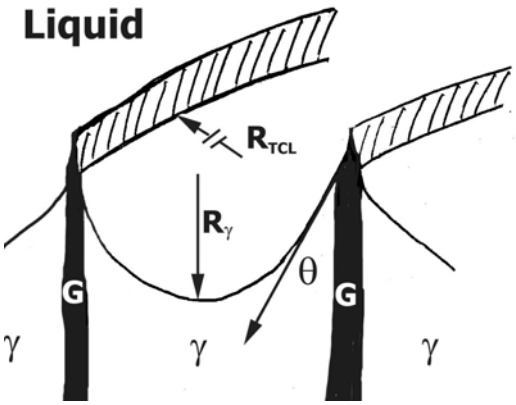


Figura 8. Tridimensional sketch for the γ/G/l interface showing: the contact angle between γ and G (θ<π/2). R_{TLC} curvature radius of the TCL, and Rγ the same for the γ /l interface.

In Fig. 9 an auxiliary sketch of the forced spreading driven by capillary forces of γ is shown.

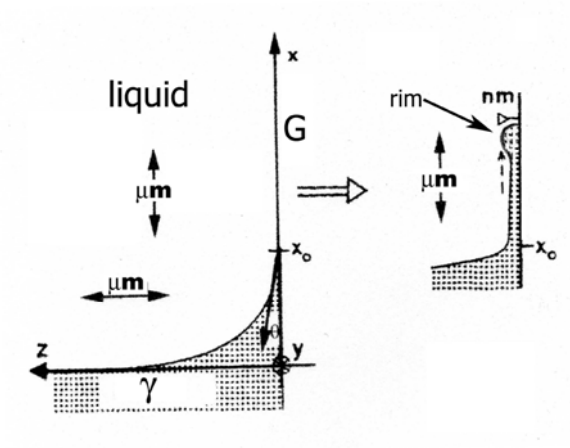


Figura 9. Heuristic analogy showing as γ climb up on a flake. It could be driven by capillary forces appearing as a consequence of different volatile solutes concentration existing between the TCL locus and bottom of the γ valleys. The ridge account for the difference of inner pressure in the solid metal provoked by high γ/l surface tensión at this level

As can be seen in the scheme of Fig. 8 the austenite "wets" graphite (θ< π/2), according experimental evidences compiled in [19] . R_{TCL} is the curvature radius of the TCL between graphite austenite and melt, and R_γ is the curvature radius of the valley by which austenite adjusts the supercooling produced by the pile up of solute. We suppose $R_{TCL} >> R_\gamma$.

It is a know fact that if flakes varieties of cast iron will be obtained the oxygen contents of the melt may be close to the equilibrium value (≅10-20 ppm)

with the atmospheric partial pressure of that gas, and the S contents ≥ 0,035 w%.

In an early work [12], we propose that graphite/ austenite interfaces in flake cast iron *must be rough* in order to preserve the strong relationship between the crystallographic growth direction of both solids relative to the externally imposed growth direction (in spite of branching and bending observed in the microstructure). It is graphically shown in Figure.10 reproduced from [12].

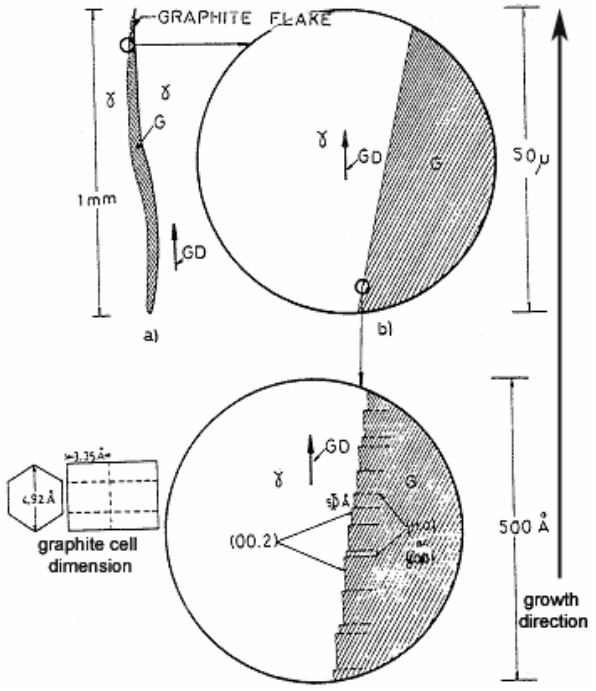


Figura 10. Growth of Graphite flake without change of cristallographic orientation. The observed deceptive curvature of the flake was fitted by a lot of steps at atomic scale making the interface rough.

There is also experimental evidence of strong adsorption of elements belonging to the IV group (S and O) on graphite austenite interfaces. As surface roughness and chemically inhomogeneous surfaces [25] are the principal sources of TCL instabilities (TCL is a one-dimension interface), we suspected that instabilities should occur where graphite, austenite and melt meet, and they would play a role during eutectic growth. To our knowledge, this factor and related or concomitant effects on the shape of neighbor two-dimension interfaces (austenite/melt and graphite/melt) are not taking still accounted for in a stability analysis of irregular eutectic growth.

On the other hand, during climbing up of fluids driven by capillary forces, at the TCL where the fluid/vapor interface meets the substrate/vapor interface, a ridge is formed [26].

Now, in order to explain our experimental evidence we shall use an analogy. This analogy was established between fluid film spreading, driven by capillary forces under thermal and concentration gradients, and the "spreading" of austenite on graphite as eutectic solidification goes on.

The situation depicted in Fig. 9) is exactly the same one that happens when a fluid climbs up the wall of a vessel by capillary forces (here we called it the substrate). If a positive thermal gradient is imposed on the substrate, in the X direction, and if one component of the liquid has a high vapor pressure (it is a volatile one), as the film spreads up by capillary, the concentration of the volatile component would be depressed by evaporation. Then, liquid vapor surface tension will rise locally and a ridge is formed at the TCL locus. This is so because the fluid compensates the difference of inner pressure in the fluid provoked by high surface stress through higher curvature.

This cylindrical ridge should be prone to suffer a Plateu-Rayleigh instability [25; p:89]in order to lower the surface/volume energy. Afterward, fingering of the film is observed [26,27]. This subsequent instability helps the system to account for dissipative processes of heat and matter. The whole process and characteristic λ is showed in the sketch of figure 11 for flake cast iron.

Another experiment, that also gives fingering of films, could be made using pure liquids, but now imposing a negative gradient in the X direction; in this way, the higher liquid vapor surface tension is again near the TCL locus (the surface tension of the pure liquid usually decreases whit temperature). In the latter example, non-compositional gradients exist and gradients of surface tension have only thermal origin. But, in both cases, gradients of surface tension produce TCL and surface instabilities.

Coming back to our eutectic system, we expect, based on equilibrium partition coefficient of O and S, that these surface-active solutes were strongly segregated to the liquid by the two solids. In particular graphite phase has practically zero admittance of solutes. As was showed , this phase is the leading one at the biphasic solid interface. So, it might be expected these solutes to be easily rejected

laterally by G. In that case, they would strongly pile up in front of neighbor γ (that also grow rejecting S and O). As a consequence, γ phase must develop a concave curvature with respect to the liquid in order to accommodate the solute supercooling.

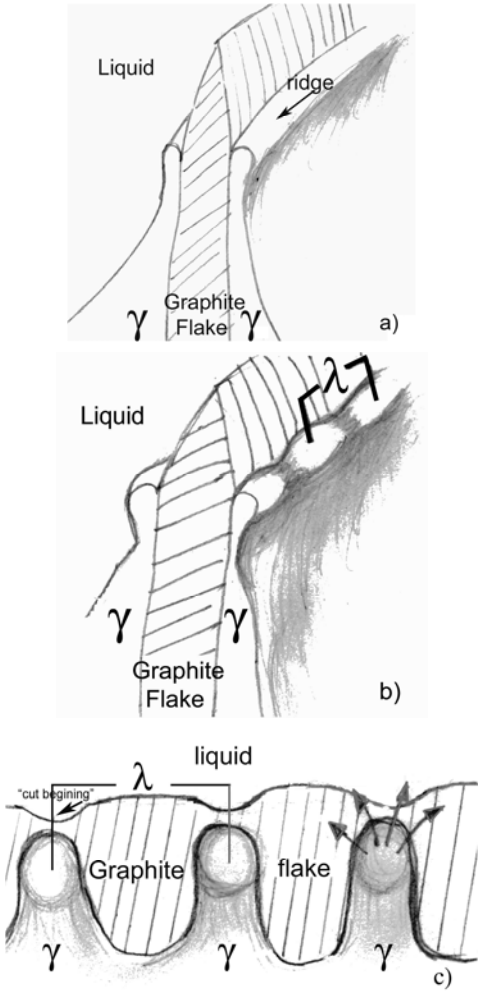


Figura 11. Sequence of increasing instability and fingering of γ: a) Marangoni flow makes the ridge, b) the ridge suffers Plateau- Rayleigh instability, c) fingering of γ and associated solute pile in front of G the beginning of branching (cut) of mother flake.

As it was mentioned, S and O have strong surface activities on Fe melts [24]. There are not data on the effect of S and O on γ / melt surface tension, but we suppose that if this solute lowered the melt vapor surface tension the same would occur in the γ / melt interface. (To support this assertion we can invoke the empirical relationship between the surface energy of a metal with his own melt and the correspondig melt/vapor: $\sigma_{sl} \cong 0{,}18\ \sigma_{lv}$;[28].

The general relationship between the surface excess $\Gamma_{S;O}^{\gamma/melt}$ of solute at the interface, the surface tension $\sigma^{\gamma/melt}$ and $a_{S;O,}$ the activity of S or O, is given by equation (1); [24].

$$\Gamma_{SorO}^{\gamma/melt} = -\frac{1}{RT}\frac{d\,\sigma^{\gamma/melt}}{d\ln a_{SorO}} \qquad (1)$$

If $\Gamma_{S;O}^{\gamma/melt}$ is > 0 indicates that the elements would be preferentially located at the interface lowering the $\sigma^{\gamma/melt}$ value.

From previous discussion, we expected that concentrations (and obviously the activity of S and O), would be higher at the bottom of the valleys of γ/melt interface than near the locus of TCL. So, if surface-active solute compositional gradient exists, an associate surface tension gradient of $\sigma^{\gamma/melt}$ must also exist. At the TCL $\sigma^{\gamma/melt}$ would be greater than the one in the bottom of the valley. Then, the difference of surface tension would drive to the formation of a ridge (Marangoni`s flow), the Plateau Rayleigh instability and fingering of the solid.

Taking into account the situation at the top of austenite fingers, we can assert that the driving force for the growth of G neighbor phase would be diminished. It is a consequence of the more efficient rejection of latent heat (that reduces locally the supercooling) and the lateral rejection of solute that increased the concentration in front the tip of G forcing it to adopt a negative curvature to accommodate the solute undercooling. So, the G phase, just in front of the tip of austenite finger, must go inward. It is also possible that local overgrowth of G, produced by γ, occurs. So, the "scissors" we mention upwards may be the metallic phase, and strips of graphite will be created.

In our opinion, there is no evidence that the flake graphite phase grows by a defects-controlled mechanism. On the contrary, we think that lamellae probably grow by diffusion-controlled mechanism [17,19]. Additionally, we think that the interface between the two solids is preserved during growth. If these situations hold, it would be natural for graphite strips to keep on growing following directions where C rich melt exists; that is between fingers of austenite. Necessarily, this implies that the daughter flake would be twisted in relation to the plane of the primitive flake. Additionally, as fingering has a characteristic dimension, the spacing of daughter flakes would be related to that. The precedent proposal explains most of the observed

branching characteristic and emphasized that the cooperation of austenite would be essential to initiate branching of graphite.

A strong dependence of the spacing whit thermal gradient is expected on the basis of precedent proposal, but its explicit form would require a stability analysis.

It was experimentally measured that surface-active solutes like S and O have a *positive temperature coefficient* for surface tension of Fe_{melt}/vapo interface. As the active solute concentration goes down, the variation of positive temperature coefficient is more pronounced [24]. Then, a non trivial conclusion of the present model is that the *positive gradient in front of the interface not necessarily implies a stabilizing effect*, especially if the surface-active solutes have a positive temperature coefficient, because, in such a situation, positive gradients may induce branching. That could explain the observed reduction of spacing with increasing positive gradient.

5. CONCLUSIONS

1. It was observed that graphite branching of graphite phase in flake cast iron proceeds in the mayor dimension of flakes.
2. The proposed faceted defect controlled growth of eutectic flake cast iron was not confirmed.
3. A new branching controlling mechanism was suggested:
   a) Solidification profiles of surface-active elements like S and O are responsible for the occurrence of surface tension gradients at the γ/l interface.
   b) Marangoni stresses, arising from those compositional gradients of surface active solutes, drive flow of matter to the TCL, building a γ ridge there.
   c) The cylindrical ridge suffers a Plateu-Rayleigh instability and triggers fingering of austenite. The driving forces for this process would be surface/volume energy decrease.
   d) Branching of graphite flake is promoted by solute pile accomplished by γ fingers
   e) On the frame of this new mechanism, strong dependence with negatives or positives externally imposed gradient should be expected.

6. REFERENCES

[1] J. D. Hunt, K. A. Jackson, *Trans. Met. Soc. AIME, 1966, **236**, p. 843.*

[2] J. D. Weeks, H. Guilmer, *Adv. Chem. Phys., 1979; **40**,, p. 157.*

[3] D. J. Fisher, W. Kurz, S*olidification and Casting of Metal, 1979,*The Metals Soc., London, *p.57.*

[4] W. Kurz, *Int. Met. Rev., 1979, **24**, p. 177.*

[5] H. A. H. Steen, A.. Hellawell, *Acta Metall., 1975, **23**, p. 529.*

[6] B. Toloui, A.. Hellawell, *Acta Metall., 1976, **24**, , p. 565.*

[7] H.Biloni, W. J. Boettinger, *Physical Metallurgy, Ch.8: Solidification, 1996,* IVth Ed., R. W. Chan and P. Haasen, North Holland, *p.763.*

[8] D. J. Fisher, W. Kurz, *Acta Metall., 1980, **28**, p.777.*

[9] P. Magnin, W. Kurz, *Acta Metall, 1987, **35**, p.1119.*

[10] P. Magnin, R.Trivedi, *Acta Metall. Mater, 1991, **39**, p.453.*

[11] P. Magnin, J. T. Mason, R.Trivedi, *Acta Metall. Mater., 1991, **39**, p.469.*

[12] A.N. Roviglione, J.D.Hermida, *Materials Characterization,1994,* **32**, p.127.

[13] A.N. Roviglione, *Materials Characterization, 1993,* **31**, p. 209.

[14] B. Lux, W. Kurz, *The solidifications of Metals, 1968,*ISI Pub.110, London, p.193.

[15] H. Fredriksson, S. E. Watterfall, *The Metallurgy of Cast Iron, 1975,* Ed B. Lux, F. Mollard and I. Minkoff, Georgy. Pub., Suisse, (fig.6 and 7) p. 282.

[16] Y. X. Li, B. C. Liu and C. R. Loper Jr., *AFS Trans., 1990.*Vol 98, **90-112**, , p.483.

[17] S.B. Subramanian, D. Key, G. Purdy, *AFS Trans, 1982*Vol. 90, **82-179**, p.589.

[18] A.N. Roviglione, J.D.Hermida; *Metallurgical and Materials Transactions B, 2002,*Vol **33 B**, p: 235-241

[19] A.N.Roviglione, J.D.Hermida, *Metallurgical and Materials Transactions, 2004,* Vol. **35 B**, 313-330.

[20] I. Minkoff, B. Lux, *Cast Met. Res. J., 1970,* ***6****, p.181*.

[21] D. D. Double, A. Hellawell, *The Physical Metallurgy of cast iron,1975,* Ed. B. Lux, I.Minkoff, F. Mollard, Georgi Puh. Co, St. Saphorin, Switzerland, p.509.

[22] I. Minkoff, *Physical Metallurgy of Cast Iron*, Cap.3, J.Wiley & Sons Ltd, *1983,* New York, p.65.

[23] A. M. cazabat, *Adv. In Colloid and Interf. Sc*., *1992;* **39**, p.61

[24] B.J.Keene, *Int. Met. Rev., 1988* Vol.*33*, Nº1,*p.1- 37.*

[25] S.Safran, *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes,* Frontiers in Physics, Vol 90, Addison –Wesley Pub. Co, *(1994)*, p.110 and 89.

[26] A. M. Cazabat, et al., *Nature,* **346**, *1990*, London 1990, p. 824.

[27] P. Carles, A. M. Cazabat, *Journal of Colloid and Interf. Sc*., *1993*, **157,** p.196.

[28] F. Delannay et al., *Review , J. Mater. Sc., 1987, Vol* ***12****, p. 7.*