LEAKAGE DEFECTS VIA BUBBLE TRAILS IN GREY IRON CASTINGS

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Abstract

Recent work with aluminum alloy castings indicated that bubbles of oxidising gases emanating from sand cores produced trails of oxide that could form leakage defects. The present work was conducted to determine if similar behavior could be observed in iron castings.

Leakage defects in large grey iron diesel engine crankcase castings were therefore opened by fracturing. The fracture surfaces were subjected to an SEM study, revealing the leak paths that were determined to be bubble trails resulting from the blowing of a core. There appeared to be two distinct types of leak structure.

1) Well-formed clusters of perhaps 10 or 20 bubble trails. Some trails were formed from films that were translucent when viewed by SEM, being only a few tens of nanometres thick and seemed likely to be amorphous, and possibly recorded the passage of single bubbles. Thicker films probably originated from the passage of multiple oxidising bubbles, and had crystallised, consisting of crystals approximately 1 μm diameter. Both thin and thick trails appeared to consist of tubes formed from films of iron silicates. These are thought to originate from fairly modest core blow events characterised by only microscopic exits at the surface of the casting.

2) Severe damage from more serious blow events more akin to volcanic eruptions, creating deep craters on the casting surface measured in millimetres. Internal features include masses of siliceous oxide slag material that was thought to be the residue of early silicate trails, plus highly damaged carbonaceous trails composed of what appeared to be graphitic films. It is not clear whether the different bubble trail compositions can be attributed to the different oxidising and reducing gases evolved by the core during the progress of the decomposition of its organic binder or whether the effect is a natural consequence of the oxidation of cast iron at different temperatures.

Introduction

Leakage defects in castings are here defined as through-wall faults sufficiently open for fluids such as air or water to penetrate the casting wall. They can occur by a number of mechanisms. These include:

- Shrinkage porosity. (The expansion of the graphite makes this source of problems unlikely for iron castings.)

- Bifilms (double films of oxide or carbon etc. folded in by turbulence during the pour), representing probably the most common source of leakage failures in castings. (Unfortunately most often mis-identified as shrinkage porosity.)

- Bubble trails. Bubbles can enter the casting because of air entrainment during the filling of the mold. However, in general, these are rather small and scattered, some of which may have the chance to float out during the time the metal is entirely molten. In contrast, outgassing from cores creates large volumes of gas and large diameter bubbles that lead to significant bubble trail defects. This paper concentrates on this mechanism.

Bubble trails were predicted to occur in castings as long ago as 1991 [1]. Figure 1 shows a sketch depicting a number of bubbles rising in a liquid that forms surface films, such as the surface oxide film in liquid Al alloy. The bubble is analogous to a balloon tethered on a string. If the bubble is small (approximately 5 mm or less) it will be unable to float upwards. Only if its buoyancy is great enough will it overcome the strength of the oxide and rise. This happens by it tearing the skin on the crown of the bubble, allowing the skin to slide around the bubble surfaces as it rises. Naturally, the oxide skin on the crown continuously reforms, so that the bubble trail is continuously generated by the ascent of an oxidising bubble, such as an air bubble.

The gathering together of the bubble skin under the bubble, to form a long, corrugated, collapsed tube (Figure 1), gives the bubble trail its characteristic 'woody' appearance when broken open on a fracture surface. Despite its extreme thinness, the oxide skin has a certain amount of rigidity, which prevents the tube from collapsing completely. As a result, a small central channel is a feature of the trail. Usually, the rising bubble bursts at the liquid surface and escapes. However, the bubble trail remains in the solidified casting. Leakage of fluids such as air or water can occur via the central core of the remaining bubble trails.
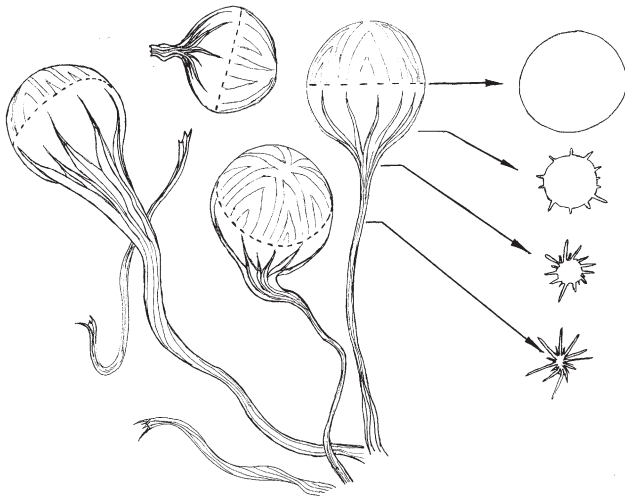
Figure 1. Pictured above, bubbles, bubble trails and the development of the corrugated, collapsed cross-section tubular form [1].

Aluminum alloy castings appear to suffer regularly from bubble trails. Many bubbles originate from the poor filling system that generally entrains significant quantities of air with the molten metal. For bubbles entrained by turbulence during the pour, the entrainment events are usually well back in the running system, so that, on emerging from the ingate into the mould cavity, the ascending bubble has its trail effectively trapped some considerable distance back along narrow channels

A second, important source of bubble trails in castings are 'blows' from cores. Such defects arise simply because cores are usually surrounded by liquid metal, heat up rapidly, and their entrapped air between grains of the aggregate, and the outgassing of volatiles from the thermal breakdown of the organic binder, can create a high internal pressure within the core. A good design of core will allow these gases to vent via the core print and so escape harmlessly into the mould. However, sometimes this escape path is inadequate, or is overwhelmed. In this case the gases will escape, being mechanically forced into the liquid metal. These bubbles effectively 'blown' into the liquid are, logically, called 'blows'[2]. It will be appreciated that bubble trails resulting from core blows are particularly serious because they arise and traverse exactly those walls of the casting that are designed to retain fluids. 'Leakers' are one of the major causes of scrap in a foundry.

Liquid aluminium alloys [3] and zinc alloys [2] have been observed to suffer from bubble trails. Although serious defects, they have a relatively simple structure and are easily explained. Bubble trails appear to have been previously observed in grey irons, but have not been recognised nor understood (they were originally thought to be some kind of segregation defect!) [4]. This short account records the first detailed observation of bubble trails in a grey iron, showing them to be significantly more complex than those in light alloys, reflecting the greater complexity of ferrous behaviour.

Method

The current samples were taken from grey iron diesel engine crank case castings that had failed the leak test, and so were scrapped. The leakage problems were found between the water jacket core and the top deck of the casting, near the top of the mould. The casting wall was only 4 mm thick at this location. The cores under this top wall were complex in shape, in general substantially thicker than the wall, being up to 100 mm thick in places. Moulds and cores were made from 55 AFS silica sand bonded with phenolic urethane resin. The poured weight of each of the castings was approximately 1200 kg. The composition of the iron was approximately Fe-3.2C-2.0Si. A standard leakage test was carried out by immersing the casting in water and pressurising with air. The point from which issued the stream of bubbles was marked on the casting and a small sample of the casting, approximately 10 mm around the defect, was excised by mechanical saw. The castings were subsequently cut by further mechanical sawing to within a few millimeters of the defect from either side and finally fractured through the defect with the impact of a hammer. Each fracture surface was found to contain a single leak path clearly identifiable with the unaided eye. Fracture surfaces of defects from six castings were examined and found to fall into two clearly distinct groups, denoted here A and B. Thus two typical Type A samples and one typical Type B sample are described in this short account.
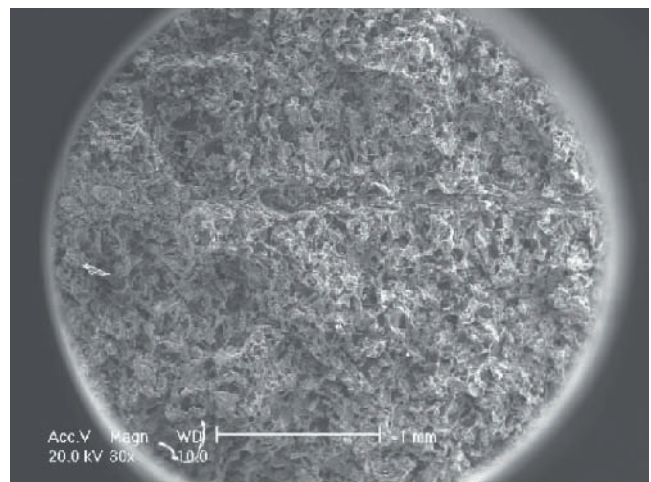

Figure 2a (Type A defect; Casting No 1) Secondary Electron (SE) SEM Image of bubble trail in casting (circular frame is the complete field of view, approximately 3.5 mm in diameter, showing most of the thickness of the 4 mm thick casting wall).
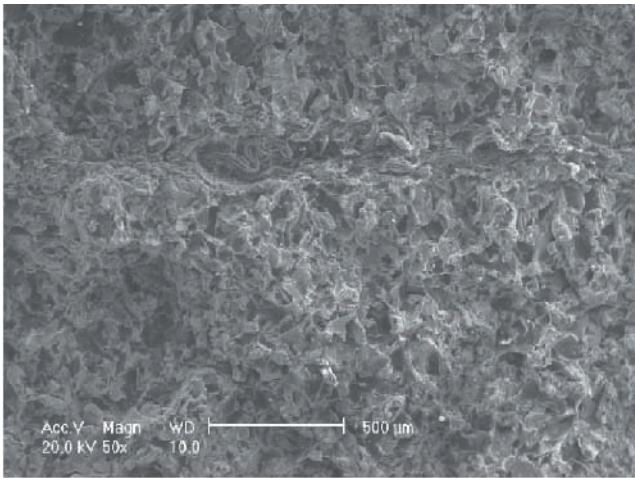
Figure 2b (Type A Defect; Casting No 1) Closer view of figure 2a.
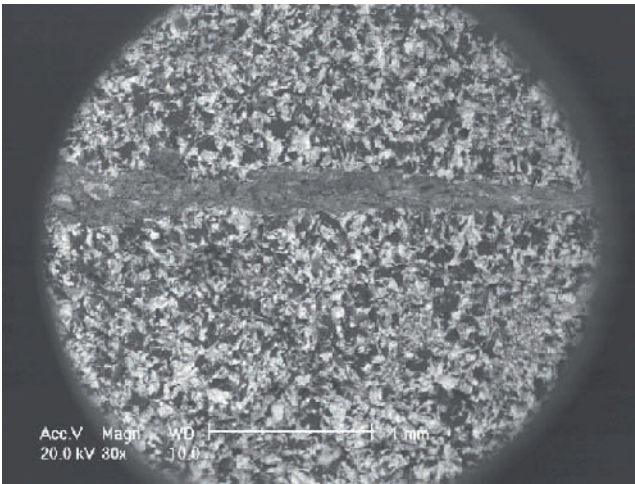

Figure 3a. (Type A Defect; Casting No 1) Back Scattered Electron (BSE) SEM image of Figure 2a illustrating the light element content of the bubble trail.
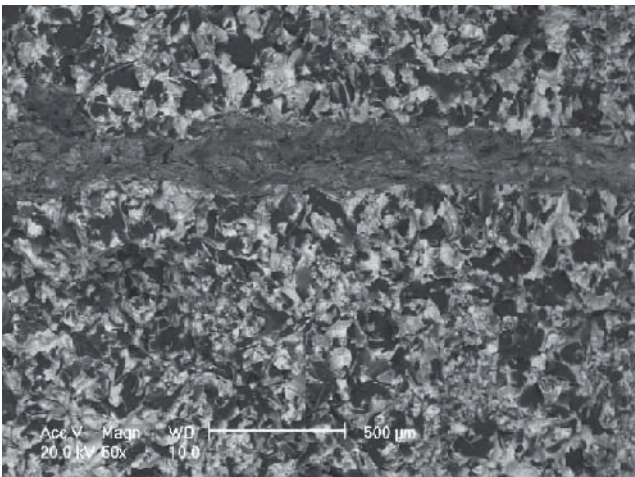

Figure 3b. (Type A Defect; Casting No 1) A closer view in BSE mode corresponding to Figure 2b.
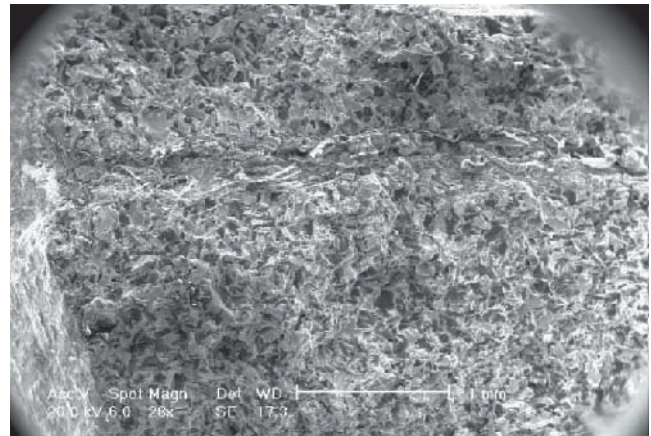

Figure 4a. (Type A Defect; Casting No 2). Secondary electron image of the fracture surface containing the leak defect traversing the complete 4 mm thick casting wall, showing the leakage hole only approximately 300 μm diameter emerging at the casting surface.
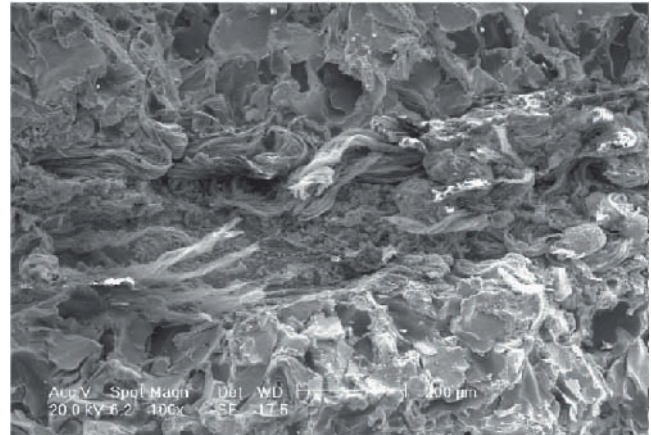

Figure 4b. (Type A Defect; Casting No 2) showing the irregular grouping of bubble trails near the centre of the leak path.

Observations

With regard to the appearance of the casting to the unaided eye, Type A samples showed little in the way of characteristic features on the surface of the casting, the leaks evidently being holes so tiny that they were hardly visible to the unaided eye. Type B sample had a clear crater-like depression several millimetres in diameter on both the inner and outer surfaces of the casting wall, clearly indicating the site of a major leakage defect.

The fracture surfaces were studied by SEM. For the first Type A sample, an overall view of the fracture, showing the defect traversing the whole of the 4 mm thick casting wall is seen in Figures 2 and 3. In Figure 2, the SEM image uses secondary electrons (SE) so that the path of the defect is only just discernible. (It is to be noted that the defects are shown
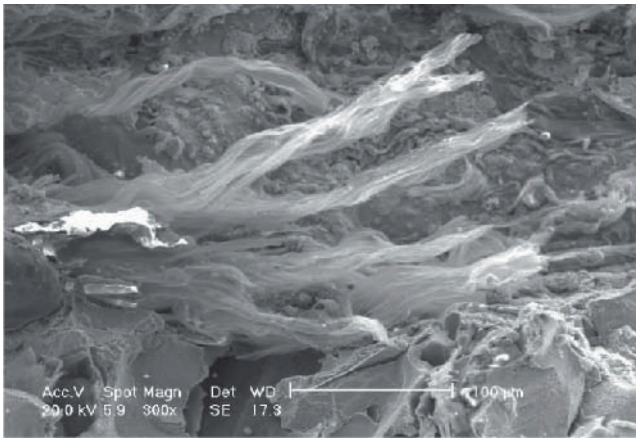
Figure 4c (Type A Defect; Casting No 2) A closer view of sample 1 illustrating the twisted form of some trails.
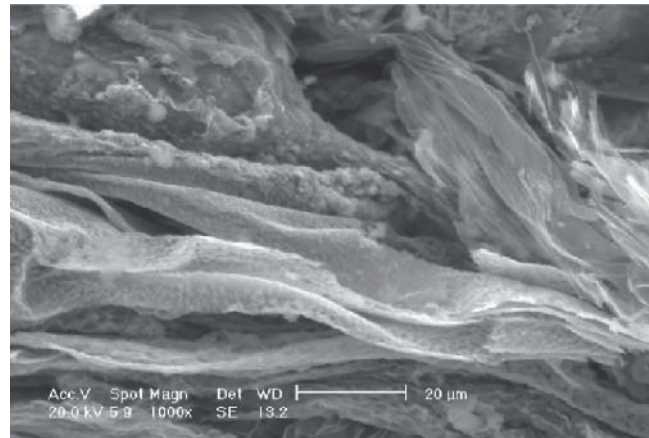

Figure 4e (Type A Defect; Casting No 2) Images of thin translucent and thicker granular films.
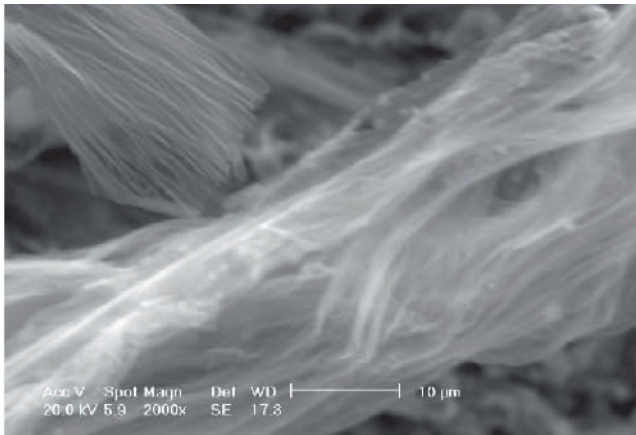

Figure 4d (Type A Defect; Casting No 2) A close-up view of translucent fluted trails (foreground trail is necessarily out of focus).
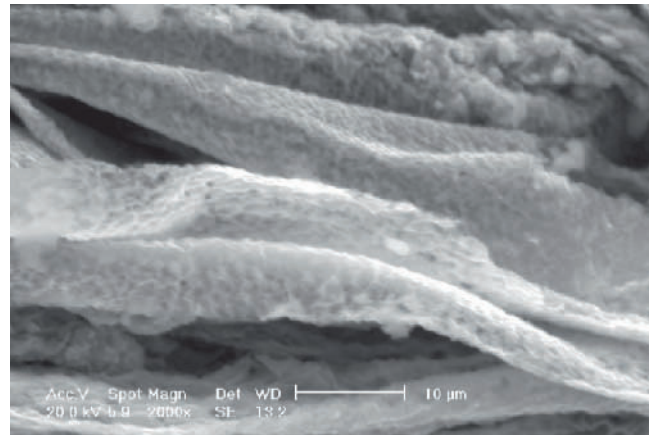

Figure 4f (Type A Defect; Casting No 2) A closer view of an apparently recrystallised silicate film, showing crystals close to 1μm in diameter.

horizontal for convenience of 'landscape' presentation, but in the casting are oriented substantially vertically.) The near-invisibility of the defect is a cautionary warning: these defects appear to have been consistently overlooked for years, despite the huge research efforts expended on cast irons.

Figure 3 shows the same fields of view but imaged by back-scatted electrons (BSE), to reveal the defect in its entirety with much greater clarity. Also, of course, the defect is further revealed to consist largely of light elements (lighter elements scatter electrons only weakly, giving a low signal count, and thus appear dark in the image).

Figure 4a shows the complete length of the defect through the 4 mm thick wall of Casting No. 2. The point at which the leak path emerges at the outer face of the casting is clearly seen to be only approximately 300 μm diameter, and so barely visible to the naked eye. Figures 4b to 4f show a series of close-ups of the films that constitute the tubular bubble trails.

Figures 4b and 4c indicate that the leak path is formed from a cluster of perhaps 10 or 20 separate bubble trails, many of them spiralling, assuming to reflect the often-observed spiralling mode of rise of bubbles in a liquid (an effect foreseen years before in the sketching of Figure 1). The extreme thinness of the films, allowing them to be translucent to electrons, can be noted in Figure 4d. It is estimated that the thinnest films are probably only tens of nanometres thick. The longitudinal tracery of fine folds, or creases representing straightened folds, seems characteristic of the thinnest films.

A mix of thin and thick films is seen in Figure 4e. The thicker films are opaque when viewed by SEM, and appear significantly more granular. In Figure 4f, the granularity is seen to be of the order of 1 μm, and it seems likely that the films themselves are approximately this same order of thickness. An interesting detail in 4e is a feature suggestive of a small explosive event in the upper part of the image.

Figure 4g shows a thin film edge-on, so that its thickness can be estimated to be, at most, approximately 50 nm. The EDX analysis, typically seen in Figure 4g, convincingly indicate that this film is composed mainly of silicon and oxygen, possibly with some iron and even lower amounts of manganese. Thus it seems most likely that the thin films in Type A defects are an iron silicate, possibly containing a little Mn in solution.

The white patches on parts of the films seen in Figure 4h appear to be lower in Fe than neighbouring regions, although it is recognised that comparative analyses of such thin material is likely to be significantly influenced by signals from the surrounding matrix.

Finally, in Type A samples (Casting No. 2), a number of exudates of matrix iron were found entering the bubble trails (Figure 4i).

Type B samples (typified here by Casting No 3) appeared to have a significantly more serious leak defect. Figures 5a and 5b illustrate the complete wall thickness, showing the craters on the inner and outer faces of the casting to be several millimetres in diameter. In addition, the internal volume of the defect is of the order of a few cubic millimetres.
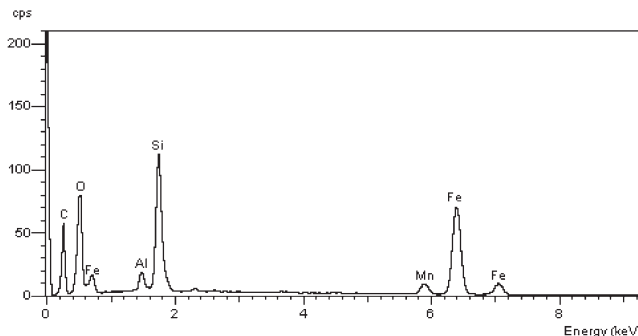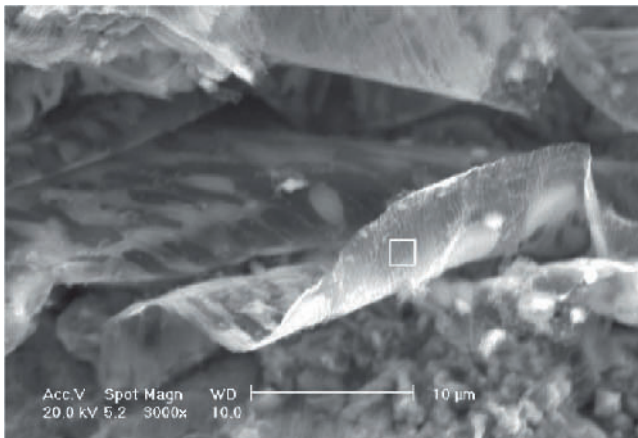

Figure 4h. (Type A Defect; Casting No 2) A spectrum from 'A' sampling the main area of the silicate film showing it to be relatively high in Fe, contrasting with the low content in the white spot region 'B'.

Figure 4g. (Type A Defect; Casting No 2) A thin, fluted film seen edge-on to reveal its thickness in the region of 10-20 μm. The associated spectrum indicates that the film is an iron silicate.
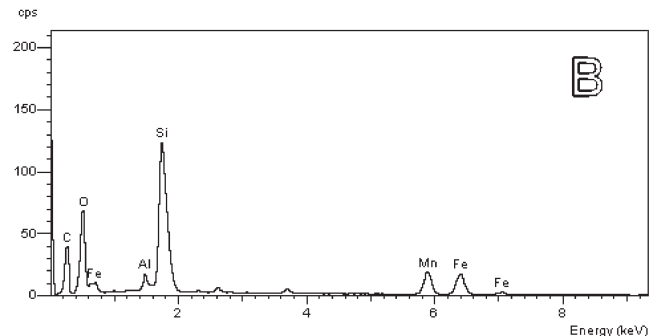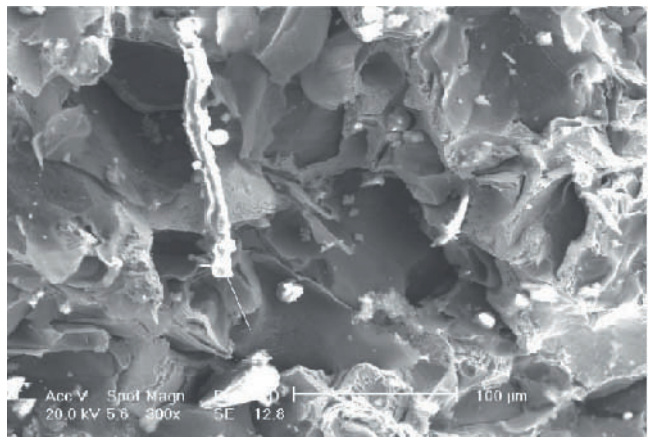

Figure 4i (Type A Defect; Casting No 2) An iron matrix extrudate, extruded into the void created by the leak path.
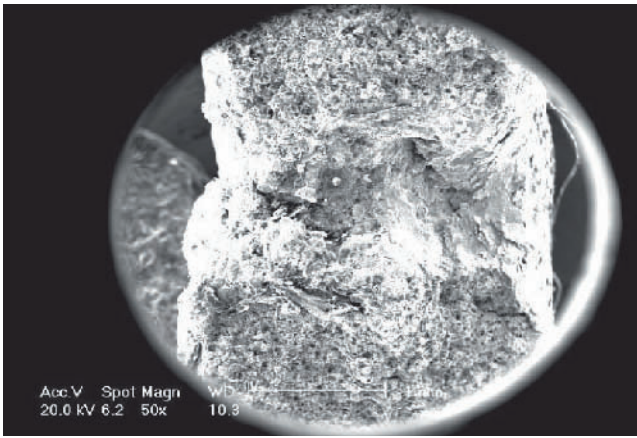
Figure 5a (Type B Defect; Casting No 3) A secondary electron SEM image of a cavernous leakage defect.
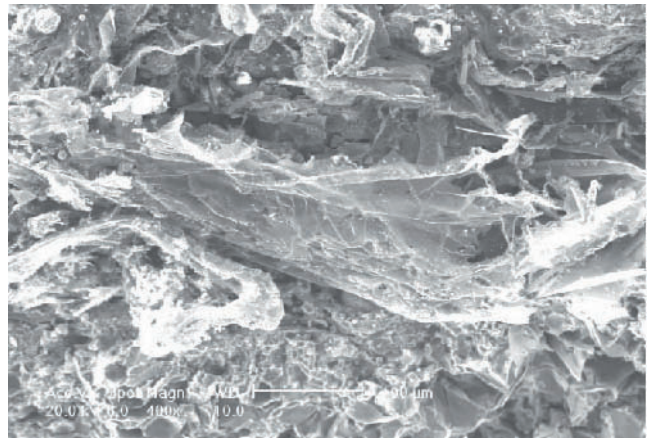
Figure 5d Close-up of 5c.
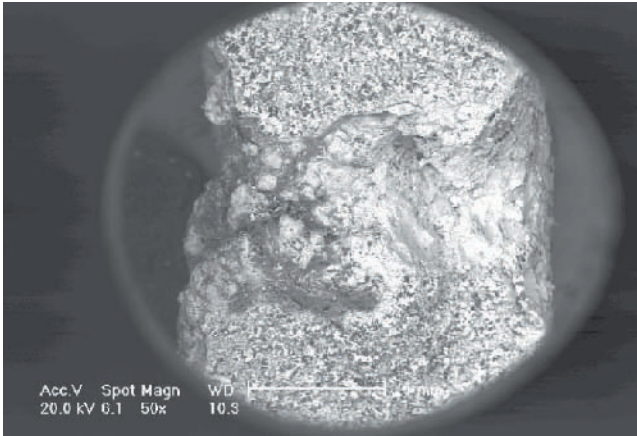
Figure 5b (Type B Defect; Casting No 3) The BSE image of the leak defect seen in Figure 5a.
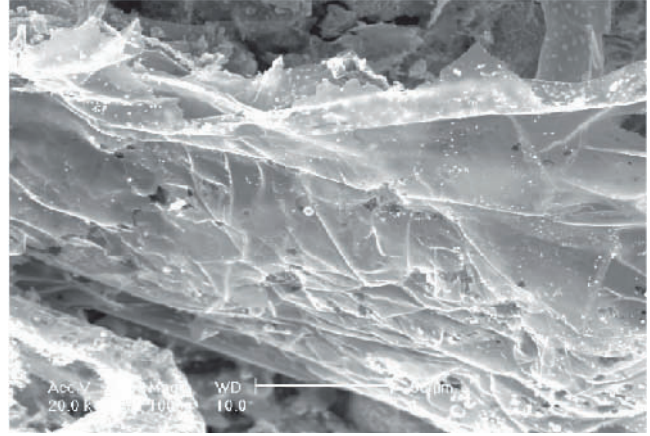
Figure 5e. Close up of 5d.
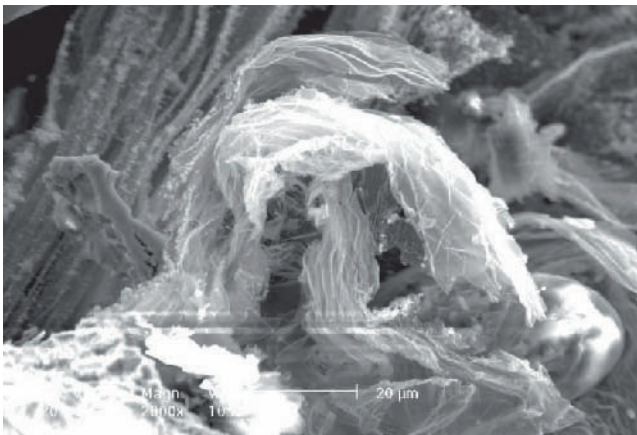
Figure 5c (Type B Defect; Casting No 3) Distorted remnants of carbon bubble trails (SE image).
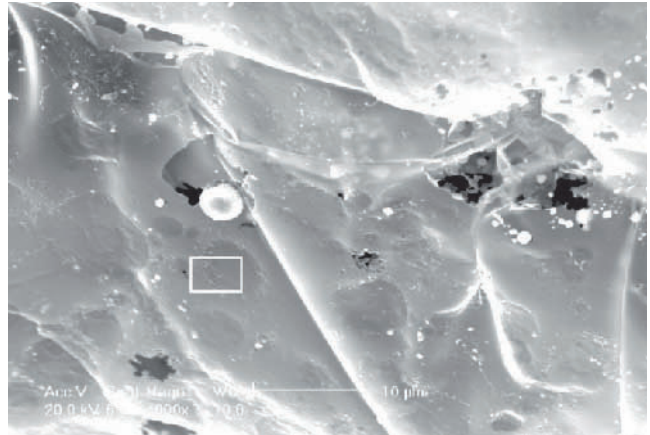
Figure 5f. Close-up of 5e.
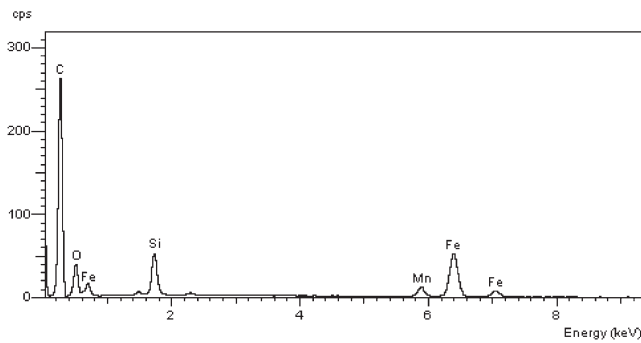
Figure 5g. Spectrum from rectangle on Figure 5f, showing the film to be high in carbon.
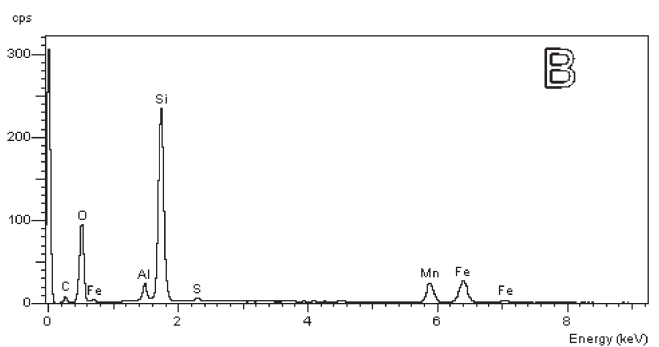
Spectrum B indicates that the irregular mass is probably composed of a silicate slag containing Fe, Mn and Al.

Spectrum C of matrix, confirming it to be mainly Fe, with some Si and lesser impurities.

Figure 5h. (Type B Defect; Casting No 3)
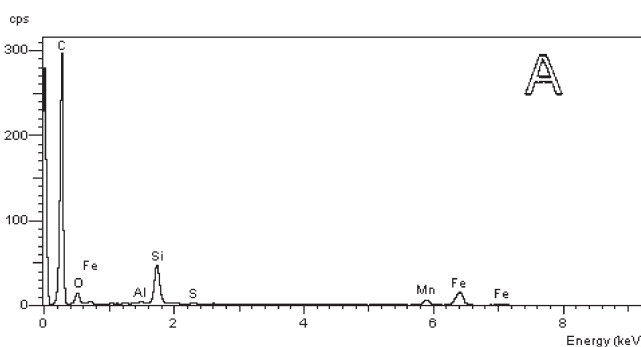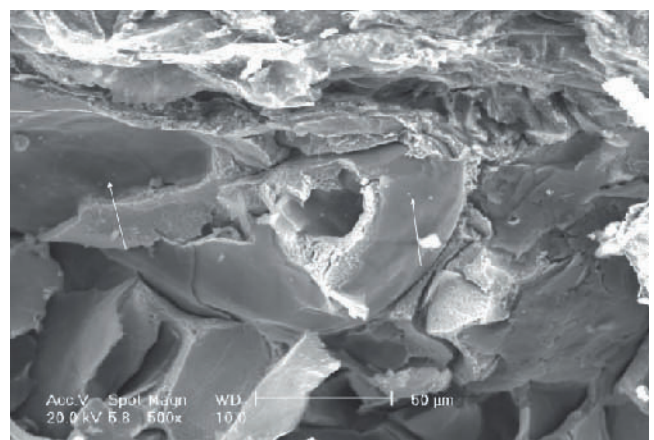
Spectrum A shows the bubble trail film to be nearly pure carbon although it is possible that some Si may be present (since the Si signal is relatively high compared to other signals such as Fe and Mn that almost certainly originate from the underlying matrix).
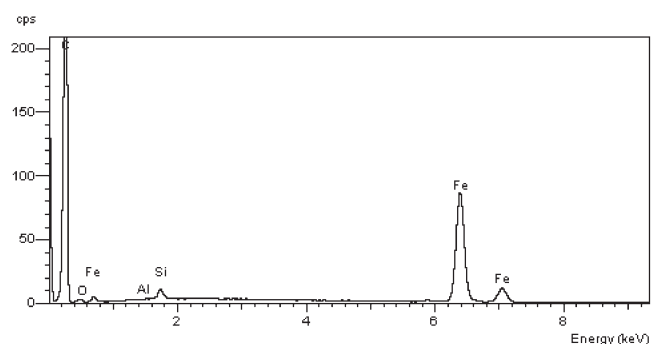
Figure 5i. Analysis of a graphite flake to confirm the sensitivity of the carbon response.

Small regions containing residual bubble trails were noted as seen in Figure 5c. These regions exhibited signs of considerable damage. One fragment of film seen in Figure 5d is shown in successively closer views in 5e and 5f. This film is significantly flatter than those observed for Type A films. The film appears to be mainly composed of carbon (Figure 5g). In other areas, the mixed scene portrayed in Figure 5h shows a more convoluted bubble trail film that is also appears to be composed mainly of carbon. The light-coloured mass in the centre of the image appears to be an oxide slag, composed mainly of a silicate with perhaps a small content of Fe and Mn. The smooth feature on the right appears to be the metallic iron matrix. For good measure, the carbon response was satisfactorily checked by analysis of a graphite flake (Figure 5i).

Discussion

The presence of extrudates of iron (for instance Figure 4i), forced into the space created by the bubble trails during the solidification of the iron and the expansion of its graphite phase, confirms the fact (if confirmation were needed) that there is an open volume into which extrudates are free to extrude, so confirming the likelihood that the observed features actually do form a relatively open channel that could cause a leakage problem.

Prior to considering the features of the defects further, it seems useful to consider first the possible phases of development of the gases produced by the out-gassing of the core. The first gases from the core will be largely air, expanding as it heats up between the grains of the aggregate. However, water vapour will also be included rapidly as the temperature of the core rises to 100 C. Water vapour will then continue to emerge at this temperature until the core surface is substantially dry, which would be expected to take time of the order of a minute or so, noting the substantial thickness of the core in places. This early phase of outgassing will therefore be expected to consist mainly of oxidising gases.

After this, as the core heats to temperatures in excess of 200 to 300 C the organic binder will start to decompose, giving off a succession of hydrocarbon volatiles. A number of the hydrocarbons will, in turn, decompose (the technical term is 'pyrolyse', being a breakdown of the organic molecular structures as a result of heat, but not involving burning as in normal combustion) further on contact with the extremely hot surface of the liquid metal, breaking down to carbon and hydrogen. The carbon formed in this way is well known in the iron casting industry, being known as *lustrous carbon*. This carbon has a characteristic pyrolytic form and is precipitated on the liquid metal surface. It is quite distinct from the carbon in the form of graphite crystals precipitated on the solid surface of iron, often on the interior surface of pores and voids as a result of diffusion of carbon in solution in the solid matrix during the cooling of the solidified casting.

Thus it is to be expected that a single early bubble, or small burst of bubbles, issuing early from a core will be highly oxidising, consisting mainly of air and water vapour. Thus any bubble trail would be expected to consist of some kind of oxide.

Single bubbles will be expected to leave a single bubble trail consisting of an extremely thin oxide film. However, the repeated flow of a succession of bubbles through a single bubble trail, as balloon-like swellings sliding up an expandable tube, is expected to greatly thicken the walls of the tube. Thus the appearance of some extremely thin, translucent films, apparently only tens of nanometres thick, appearing alongside thicker, granular or crystalline films (Figure 4e) is to be expected. This mixed behaviour, with many bubbles taking the same paths, whereas others breaking away to follow individual, nearly parallel paths, has been observed in real-time video recordings of the formation of bubble trails in Al alloys [2]. Furthermore, the dynamics of the growth and transformation of oxide films in light alloys seem analogous to the present circumstances: alumina or magnesia films on molten light alloys form initially as thin, amorphous (glassy structure) structures. As they thicken and/or as time passes, the films subsequently transform into a variety of different crystal forms [2]. By analogy with light alloy behaviour therefore it seems likely that the thin films are glassy and the thicker films are crystalline.

Figures 4g and 4h, together with their associated spectra, clearly reveal the composition of these bubble trails to be characteristic of a silicate glass (high in Si, O possibly with some Fe and Mn). The thin films are translucent, again emphasising their thinness and their possible glassy nature. As a silicate, the glass-like nature of the films is understandable, as is the appearance of the brittle fractures to the ends of the broken tubular trails as seen in Figure 4c. These brittle glassy shards are likely to have formed during the sample preparation, at the instant of the breaking open of the sample to reveal the leakage defect.

The white patches observed on some of the films seen in Figure 4h are interesting. An examination of the FeO-SiO_2 phase diagram shows that FeO-SiO_2 materials containing greater than 37w/o SiO_2 will be present as two phases, an FeO-SiO_2 phase (with about 37w/o SiO_2 and 63w/o FeO) and an essentially pure SiO_2 phase. Another possibility is a pure FeO phase and a 30w/o SiO_2 phase. The spacing between patches of segregates is in the region of 10 micrometers, and is of the order to be expected from diffusion distances in these conditions, suggesting an evolution of the silicate chemistry towards an equilibrium structure. (However, it should perhaps be recorded that in other SEM studies [5] of iron-rich compounds in cast Al-alloys, white areas appear to be associated with some kind of atmospheric corrosion that occurs on prepared metallographic specimens over a period of several days or weeks. It is not clear whether a similar effect may have occurred here.)

The silicate trails in Type A defects (Figure 4g and 4h) contrast with trails in Type B defects seen in Figures 5g and 5h that appear to consist mainly, and probably exclusively, of carbon, and seem likely therefore to be graphitic. The film seen in Figures 5d to 5f is substantially planar, and may be a remnant of the large bubble trail that surrounded the out flowing jet of carbonaceous gases in Type B events. For the smaller Type A events the only films that were observed were all of cylindrical tubular form.

The observations of these two distinct types of leak structure are suggested to be rationalised and summarised as follows.

- *Type A Defects*. The defects consist of well-preserved bubble trails formed from iron silicates in clusters of perhaps 10 to 20 or more individual trails. The trails are a mix of thin and thick varieties. The thin trails appeared to consist of translucent films of glassy silicates approximately 20 to 100 nm thickness. These are thought to record the passage of only single bubbles. The thicker films appear to be of the order of 1 μm thick and consist of crystals of the order of 1 μm diameter and seem likely to have formed from the repeated passage of a number of bubbles along the same trail. The total cluster of trails represents a relatively minor outgassing event, emerging at only a microscopic exit at the surface of the casting

- *Type B Defects*. These defects represent severe damage from more serious outgassing events. The phenomenon seems more akin to a volcanic eruption, creating at the casting surface deep craters, having widths and depths measured in millimetres, which are easily visible to the unaided eye. In addition, a significant volume of internal material appears to have been subjected to a kind of churning action. It seems likely that in conditions of the out-pouring of huge quantities of gas, individual bubbles do not form, the flow being continuous, like a jet. The highly energetic churning of the surrounding matrix creates masses of siliceous oxide slag material, some of which could be the residue of the initial silicate trails. As the evolution of oxidising water vapour is replaced by products of pyrolysis of the organic binder, the trails are now formed by decomposition of these carbonaceous volatiles, creating carbon films analogous to the well-known lustrous carbon films commonly seen on the surfaces of grey iron castings. Even so, these films are in turn mechanically damaged by the force of the outgassing flow, as is seen in Figures 5c and 5d.

Although the chemistry of the bubble trails is described above in terms of the change of the composition of gases, from oxidising to hydrocarbon-rich, there may be an alternative explanation in terms of the rate of reaction of constituents of the melt [3]. There are good fundamental reasons why carbon oxidises first at high temperature, leaving oxides of silicon and manganese-rich films. In contrast, at lower temperature, manganese and silicon oxidise first, leaving carbon to oxidise last, thus favoring carbonaceous films. The choice between these explanations remains to be clarified by future research.

The outstanding unresolved question regarding both types of trails is why the trails are detached from the walls of the matrix, and from each other. (In contrast, the trails studied in Al and Zn alloys are, as would be expected, firmly attached and integral with the matrix alloy.) It is proposed that the detachment of trails from the metal matrix may be a special feature of cast irons. This aspect is probably the central most difficult concept of the whole of this research. It is not easily explained and may take much more research to clarify the mechanism.

A possible mechanism appears to be that parallel bubble trails would co-operate, bunching together to exclude liquid iron. Such an effect is to be expected since they would first be created closely adjacent, and would actually be in intimate contact as a result of the neighboring films reducing the overall surface energy of the defect by this action (the surface energy of liquid iron is particularly high). Thus each additional parallel bubble path would travel in contact with its neighbors, and would squeeze out any liquid metal from between adjacent trails by simple capillary repulsion. Finally, when the casting has solidified and starts to cool, a solid state graphite film would start to form around the outer limits of the bunch of trails. Such free surfaces are expected to be favoured substrates because they allow unrestricted volume expansion for the precipitation of graphite. The layered structure of the graphite crystal, with its (0001) plane parallel to the wall of the defect, would allow easy detachment of any surface contamination such as a glass or a pyrolytic carbon. Thus the outer trails would be released by decoherence from the matrix. Having decohered from the matrix, their decoherence from each other is to be expected because the films would have been solid at the time of their formation. The variously different temperatures and coefficients of thermal expansion would aid this disengagement process. (One can imagine the microscale groaning, stuttering and pistol-shot cracking noises.)

This decoherence of even graphite from itself, but graphite formed in different ways, is commonly observed as on fracture surfaces of ductile iron spheroids, from which, temper graphite deposits (precipitated during cooling or heat treatment) break off from the as-solidified graphite spheroids as fractured hollow shells [6].

Petrzela [7] had demonstrated that the lustrous carbon film is formed by the decomposition ('cracking') of carbonaceous gases on extremely hot surfaces [3](such as the surface of the liquid iron but not on the rather cool surface of the sand mold). The subsequent finding by Naro [8] of large areas of the film attached to the surface of the sand mold means that the film that originally formed on the liquid iron, must

have detached from the casting and adhered to the mold. The transfer confirms the ease of the decoherence phenomena, even though the relative smoothness of the casting, and roughness of the sand mold will assist.

The detachment of both oxide and carbon types of trails from the iron matrix appears therefore to be not only reasonable but to be expected. This feature of detached and separated trails may be a unique feature of cast iron leakage defects.

Conclusions

1. Bubble trails have been observed in grey cast irons for the first time; their presence revealed as leakage defects resulting from the outgassing of poorly vented cores.
2. Bubble trails in cast irons may be unique because of their detachment from the matrix alloy.
3. It seems that in the case of relatively small leakage defects individual bubble trails can be formed from silicate films by oxidising core gases.
4. More serious out-gassing problems resulting from jetting of core gases causes significant additional damage including the in-situ creation of an oxide slag by oxidation of the matrix. Remnants of bubble trails constituted of carbon films are also observed.

Acknowledgements

References

1. J Campbell "Castings" 1st Edition 1991 pp 21-24.
2. J Campbell "Castings" 2nd Edition 2003 pp 50-53, 156-160.
3. M Divandari and J Campbell; Trans AFS 2001 <u>109</u> 201-212
4. K-H Caspers; AFS International Cast Metals Journal 1980 <u>5</u> (1) 20-22.
5. X Cao and J Campbell; University of Birmingham, UK. Unpublished work 2002.
6. Y Kuroda and H Takada; AFS Cast Metals Research Journal 1970 <u>6</u> (2) 63-74.
7. L Petrzela; Foundry Trade Journal 1968 October 31, 693-696
8. R L Naro; AFS Transactions 2004 <u>112</u> 527-545.

NOTE FROM EDITOR:

We would like to thank Professor Campbell in assisting with the inauguration of the *IJMC* with this Keynote Paper. As you will note in the following pages, we have included the technical review and discussion between the reviewers and author. We feel that this adds a unique and informative perspective to this publication. We encourage continued dialogue and comments from our readership and will publish this dialogue in subsequent editions.

Technical Review & Discussion

**Leakage Defects via Bubble Trails in
Grey Iron Castings
John Campbell, University of Birmingham,
United Kingdom**

Reviewer: It is obvious that the bubbles would have to be introduced into the iron before skin formation occurs. What should be stated about the gases that evolved during the filling of the mold cavity (the region of concern appears to be toward the upper segments of the casting as it is poured)?

Author: It is correct that bubbles have to be introduced into the iron before skin formation occurs. Mold gases are of no direct concern since they are free to diffuse away through the sand mold.

Reviewer: Lustrous carbon deposition is not limited to the decomposition of hydrocarbons, but due to the fact that in cast irons any free surface will serve as a site for lustrous carbon to form absent any oxidizing atmosphere (O_2, CO_2, H_2 etc.) as C diffuses to those surfaces and is retained by lack of oxidation at that surface.

Author: This is not true. The carbon that is commonly seen to form by solid state diffusion to solidified free surfaces of cast iron is graphite. Lustrous carbon is not graphitic. It is a pyrolytic form of carbon created only on extremely hot surfaces by the pyrolysis of hydrocarbon gases (there is no driving force for carbon to diffuse out of the melt to the liquid surface because the carbon is under its solubility limit and so in a stable form in the melt). Lustrous carbon films are often seen to be detached from the iron after solidification is complete, whereas the graphitic films appear to be firmly attached to the matrix.

Reviewer: The writer should become familiar with the concept of reoxidization of ferrous melts as characterized by free energy diagrams, wherein C is oxidized preferentially at higher temperatures and at lower temperatures Si, Fe and Mn are oxidized. This seems to explain the oxides the writer observed in the bubble trails.

Author: This is a potentially useful point. The writer has overlooked this possible contribution. (He is not ignorant about the conditions for the oxidation of elements in cast iron, as described in the author's book, "Castings 2nd Edition" published by Elsevier 2003, particularly pages 156 to 163 that deal with these matters.) These considerations refer to equilibrium conditions which may be far away from the dynamic situations considered in this paper. Even so, there may be some contribution from this source, and the Abstract and Discussion have been expanded to include this potential contribution.

Reviewer: The role of out-gassing from poorly vented cores must be explained more fully, particularly in relation to mold filling, gases evolved during mold filling, solidification time of casting sections, etc.

Author: This whole subject is given what I think is a good coverage in "Castings 2nd Edition" pages 200 to 204, and contrasted with gas porosity of other forms in the whole of Chapter 6.

Reviewer: *Line 17 says*: *"reducing gases evolved by core during the progress of the decomposition of its organic binder"* …suggest the author add the following "and reaction with the carbon in the iron."

Author: I find it difficult to envision that carbon in the iron plays any significant part. The deposition of carbon from the breakdown of carbonaceous gases on to the surface of the melt will drive the carbon diffusion gradient inwards, from the pure carbon deposit into the liquid surface, to supersaturate the liquid locally immediately under the surface. This supersaturation will of course diffuse away continuously into the bulk of the melt, while being replaced by inward diffusing carbon from the carbonaceous surface film formed by the breakdown of the carbonaceous gases. Hydrogen will also be expected to join this general inward diffusion as another breakdown product from the environmental gases.

Reviewer:

- Paragraph 11 says: "*Small regions containing…*" Reviewer Comment—add to text-"graphite – carbon films commonly associated with H_2".

- Paragraph 10 says: "*Type B Defects*" Reviewer Comments—Graphite film possibly from eutectic reaction where gr + γ come out of solution simultaneously in a lamellar configuration! Related to H_2 gas defects?

- The last paragraph says: "*The presence of a graphite film would explain…*" Reviewer Comments— unique to the eutectic solidification of cast iron with 2 constituents precipitating simultaneously gr + γ !

Author: These carbon films are not the graphitic films commonly seen formed on the solidified iron. They are pyrolytic carbon films formed from hydrocarbon gases decomposed by the extreme temperature when in contact with the liquid iron surface. In this situation the hydrogen also released in the decomposition of the gases is probably not especially relevant to the ensuing processes. This difference in the two distinctly different types of carbon film is now explained more carefully in the Discussion.

Reviewer: My compliments to Professor Campbell for offering such a well thought out explanation for leak conditions that have plagued cast iron producers who provide quality cast iron products for engineered purposes such as engine blocks. Professor Campbell presents an interesting argument concerning the cause for leakage in those applications where different fluids exist in different compartments of the casting. His hypothesis concerning the formation of graphite films is of particular interest since the graphite film has been commonly associated with the formation of hydrogen gas and hydrogen/nitrogen gas defects. These graphite films are commonly associated with shrinkage defects in gray cast iron as well and are frequently attributed to the fact that the defects occur at thermal centers where partitioning coefficient justifies the presence of hydrogen and hydrogen/nitrogen gases in the last to solidify metal.

Author: Please note that the graphite film commonly seen on the surface of shrinkage pores is expected to be graphite formed in the solid state, and thus distinct from a pyrolytic film formed on the liquid surface.

Reviewer: Out gassing from cores and chemically bonded sand molds is a known source for the gases that form these thermal center gas induced shrinkage defects. Reviewing the literature also generates considerable information that substantiates the formation of carbon monoxide gas defects that are associated with iron/silicon/manganese oxides just as Professor Campbell discusses. In fact the literature goes farther so as to identify the oxide that causes the reaction with the carbon in iron to form carbon monoxide as Fayalite, a specific iron-silicon oxide. Of course, one of the sources of the carbon can be the different hydrocarbons in the binder systems in the sand. The second source for the carbon that is the source of the reaction to form the graphite films and the carbon monoxide has been attributed to the carbon in the cast iron just as Professor Campbell considers in his discussion.

Author: I regret to say that I have misgivings about the large section of literature that describes CO gases that are purported to be generated by reaction of fayalite with alloyed carbon. In my research of the literature, in all cases these casting samples were generated by pouring in more-or-less turbulent ways. Thus all these samples of iron would almost certainly have contained entrained air bubbles, possibly even masses of air bubbles. Thus the finally observed defects in my view are almost always residual air bubbles (these never occur if the mold is filled without turbulence). Thus the fayalite is the oxidation product of an air bubble entrainment process (not the initiator), and the oxygen of the air in the bubble will certainly react to create CO. The residual contributing gas will of course be nitrogen (and nearly always some hydrogen which seems always to be present to some degree). In a way, the fayalite is a kind of slag residue

formed in situ (not a slag phase carried in from the ladle) by the copious oxidation reactions as a result of the admixture of air. The fayalite is probably the whole mass of bubble trails and bifilms raveled into a compact mass that appears as a new phase in the structure.

Reviewer: Taking Professor Campbell's thinking one step further and combining this technology with the carbon monoxide work currently being conducted with AFS sponsored research, interesting models of the mechanisms for the formation of carbon monoxide and graphite films can be developed. Since all cast irons that solidify in the stable iron-carbon system form a eutectic, and since the eutectic is a combination of graphite and austenite (gr + γ), it stands to reason that the graphite that comes out of solution during the eutectic will be in a laminar form, perhaps as a film as evidenced by the presence of the graphite flakes in gray iron and the presence of films on dendrite arms in the last to solidify metal. Professor Campbell indicates in his paper that cast iron has a unique characteristic that differentiates it from other metals. Indeed, the difference is in the fact the necessary presence of a graphite "film' from the eutectic reaction. It is this unique feature that significantly contributes to the observations that Professor Campbell has presented with the formation of at least the carbonaceous aspects of the bubble trails.

Author: There is much that can be said about grey iron structures. The solid-state formation of the well-known graphite layer in pores and voids in irons seems to me, having thought about the problem further, to be the cause of the detachment of the pyrolytic carbon film, since the graphite layer structure (the (001) plane being parallel to the surface of the matrix) will allow easy decohesion. I can think of no other alloy system where this decohesion of a surface film is likely to occur. The text of the discussion has been modified to clarify these points.

Reviewer: Regarding core blows, it would have been interesting if the author would have offered some solution to the problem.

Author: There are many ways to deal with core blows. These are listed in the book, "Castings 2nd Edition" published by Elsevier (page 203). The book has been available since 2003.

Reviewer: The title of the paper indicates the subject is bubble trails. However, the paper describes two effects. The second effect (Type B) "Severe damage from more serious blow events is a blow defect not a bubble trail defect as the title of the paper indicates. It is my opinion that the entire section does not belong in this paper.

Author: I have some problems with this opinion. The reviewer's point seems to be that drips from a partially opened faucet are quite different from the jet of liquid from

a fully opened faucet. *This is true. However, of course, the effects are merely the extremes of a continuum in which any intermediate case can be generated. In the case of the leakage defects in the castings reported in this paper, slow outgassing or rapid outgassing both lead to leakage defects. Both defects are the consequences of outgassing problems. Both are leaks. Whether we might or might not wish to call the B defects 'bubble trails' is, in my view, semantics.*

Reviewer: *"A second important source of bubble trails in castings are "blows" from cores".* The description indicates this explosive event mixes up the debris in the casting, including bubble trails, but it has nothing to do with the formation of bubble trails. I believe the section on "blows" should be removed.

Author: I am using the term "blow" in the sense that it is defined in my textbook "Castings 2ⁿᵈ Edition." Thus a 'blow' is any event formed by the mechanical forcing of gas into liquid metal from a sand core or mold, or from a partially sealed joint in a permanent mold etc. Thus single bubbles or continuous streams might both be described as 'blows'. This definition is used to distinguish these bubbles from those that occur from the entrainment of air or mold gases during the turbulence of mold filling or by precipitation from solution. The text has been revised to make these issues clear.

Reviewer: Figures 2a and 2b can be omitted. As indicated in the text *"In Figure 2 the SEM images uses secondary electrons (SE) so that the path of the defect is just discernible."* If it's just discernible why use the figure? Figure 3a and 3b show the defect clearly and so does Figure 4a. Figures 3a and 3b show the same thing.

Author: The comparison of secondary electron images with back-scattered electron images is a powerful research technique that is used here to good effect, illustrating that the defect is comprised of low atomic number elements (carbon and oxygen in these cases). A further important point is that metallurgists using SEMs in the common secondary electron mode have consistently missed these features. Illustrations of the ease with which important data can be missed by our experts even with the best equipment are worth emphasizing.

Reviewer: Paragraph 3. I am not sure if the explanation for the formation of thicker films is adequate. Figure 4c shows individual bubble trails. Once the bubble moves upward the trailing oxide film collapses. The laying down of the individual bubble trails prevents iron from entering the region which then produces the defect. (Author: Agreed). Looking at the bubble trails in the various figures, it seems clear that iron cannot run inside of these collapsed trails (Author: Agreed) nor can another bubble of oxidizing gas.

Author: This is almost certainly incorrect. Individual bubbles can easily pass up the original bubble trail. The trail is simply opened by the passage of the bubble like a snake swallowing a football. We have observed this many times by video X-ray radiography. In addition, there is a published photographic record of a bubble trail in zinc being reopened (page 50 of "Castings"). In addition, we know that individual bubbles do not necessarily ascend by the same route as previous bubbles, but create their own parallel path.

Reviewer: Are you saying that once a number of trails have been produced and iron is excluded from the region, oxidizing gases entering the region can react with the liquid metal envelope thus creating a bubble trail that encompasses all of those laid down earlier?

Author: I agree that you raise the central difficult concept of the whole of this research. This effect is not easily explained and may take much more research to clarify the mechanism. Having thought about the problem further since the writing of the initial draft of the paper it seems to me that parallel bubble trails would co-operate, bunching together to exclude liquid iron. Such an effect is to be expected since they would first be created closely adjacent, and would actually be expected to be in intimate contact as a result of the neighboring films reducing the overall surface energy by this action (the surface energy of liquid iron is particularly high). Thus each additional parallel bubble path would travel in contact with its neighbors, and would squeeze out the liquid metal from between the trails as it advanced. Finally, when the casting has solidified and the solid state graphite film formed around the outer limits of the bunch of trails, the outer trails would be released by decoherence from the matrix. This seems to me to encompass all the observed facts and is in line with theoretical expectations based on relative surface energies. The discussion is now modified to include these new thoughts.

Reviewer: There is redundancy in the figures and some could be omitted.

Author: Agree. [However], in a paper such as this, describing totally new phenomena, it seems to me preferable to err on the side of offering evidence that borders on the redundant, rather than being over economical.

Reviewer: Paragraph 6. *"The white patches observed on some of the films are less easily explained."* …it is not easy to imagine what segregation mechanism could operate in such thin material. An examination of the $FeO\text{-}SiO_2$ phase diagram shows that $FeO\text{-}SiO_2$ materials containing greater than 37w/o SiO_2 will be present as two phases, an $FeO\text{-}SiO_2$ phase with about 37w/o SiO_2 and 63w/o FeO and an essentially pure SiO_2 phase. Another possibility is a pure FeO phase and a 30w/o SiO_2 phase.

Author: Thank you for these observations. I shall be grateful to include these suggestions in the text. Since the film originally formed on the liquid, which would be assumed to be homogeneous, I have problems to understand how the various elements became so separated. However, the problem I refer to in the paper is the fact that the segregation (if this is what it is) is spaced over distances of the order of 10μm but the film is only around 10 nm thick. Having though further about this, there is probably not a problem arising as a result of this disparity in dimensions. The distances between patches are typical diffusion distances to be expected for these conditions. Thus an approach to equilibrium, forming the phases you propose from the equilibrium diagram seems perfectly reasonable. The text has been amended with this nice detail.

Reviewer: The last Paragraph in the paper requires further research and should be omitted.

Author: I agree that further research would be highly desirable. However, in the meantime, the publication of a suggested explanation would be reasonable (it would be called a hypothesis), even if eventually proved false by future work. This would be perfectly normal scientific procedure.