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PRINCIPLE GUIDELINES FOR NEW FERROALLOY PRODUCT DEVELOPMENTS

by

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ABSTRACT

The relationship between properties of ferrous materials and their microstructures is briefly surveyed, and the fundamental significance of heterogeneous nucleation in development of desired microstructures is emphasized. The conditions for efficient nucleation and the mechanisms involved in inclusion formation, particle precipitation and in solid state transformations are discussed in more detail. On this background possible ferroalloy product modifications and developments are viewed. It is concluded that the existing theoretical framework is relevant and comprehensive enough to serve as a sound basis for ferroalloy product research, and some approaches are briefly outlined.

INTRODUCTION

Many of the different elements to be added in iron and steelmaking is supplied through ferroalloys. Process developments and product quality shifts in ferrous metallurgy rely much on improved compositional control. This again is reflected on ferroalloys in terms of stricter quality specifications for greater uniformity and higher purity. The future role of ferroalloys has to be viewed on the background of the needs of the iron and steelmaker since further requests for alloy modifications or possible new grades clearly derive from these.It is therefore vital for any ferroalloy producer to be able to identify threats as well as opportunities arising from the continued developments and changes in iron and steelmaking technology. The impacts on the ferroalloy production line can be quite dramatic. An illustrating example is the steep decline in demand for low carbon ferrochrome with the event of AOD and VOD refining in stainless steelmaking. Another one is the development of thermo-mechanical rolling steels requiring low carbon contents, which has led to increased demand for medium to low carbon ferromanganese.

The present paper is an attempt to outline developments for improving ferrous material properties which may affect the traditional function of ferroalloys in deoxidation. The resulting ideas derive from interest in steel welding and inoculation mechanisms in ductile cast iron /1-3/, and are based on a common principle being applicable in ferrous metallurgy.

TRENDS IN IRON AND STEEL MANUFACTURING TECHNOLOGY.

Demand for higher performance materials with optimal combination of properties is steadily becoming more critical. Since microstructure determines material properties, a desired property profile is to be obtained by development of properly adjusted microstructure.

As-cast Microstructures in Steel.

As-cast steels are prime examples of materials where the properties achieved depend upon the characteristics of the solidification microstructure. With reference to Fig.1(a) coarse columnar grain structure will inevitably evolve upon solidification if potent heterogeneous nucleation sites ahead of the solidifying front are absent. In the presence of effective seed crystals fine equiaxed, delta ferrite grains form directly in the melt, as illustrated in Fig. 1(b). Examples of such active catalyst particles are sulphides with Ca and REM and carbides/nitrides with Ti,V,Nb/4-6/. They are either primary or secondary reaction products originating from ladle refining processes. Depending on circumstances, an equiaxed grain evolution may completely override the inherent columnar grain formation with the beneficial result of improved hot ductility, hot cracking resistance and reduced segregation /5,6/. The latter effect derives from the associated reduction in primary and secondary dendrite arm spacings, (λ_1 or λ_2), which together with element diffusivity (D) determine the soaking time (t_{hom}) necessary for homogenisation:

$$t_{hom} = k_1 \frac{\lambda^2}{D} \tag{1}$$

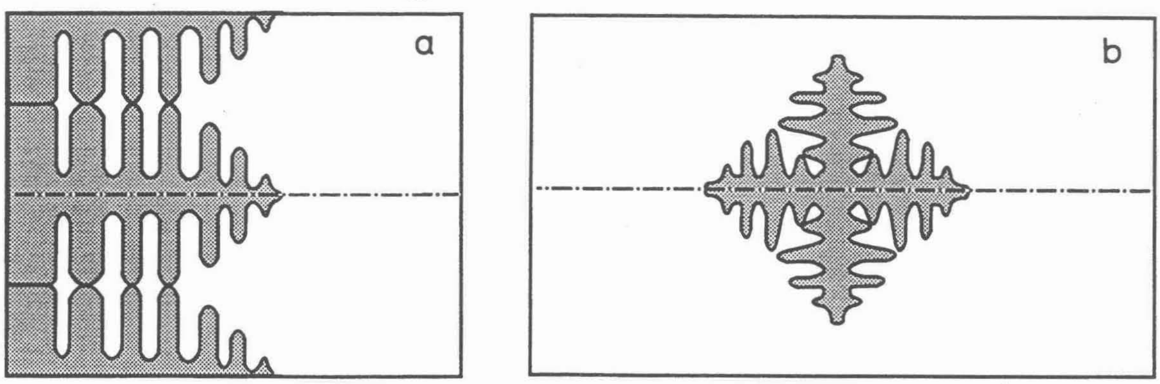

Figure 1. Schematic diagrams showing different dendrite growth morphologies in castings: a) columnar dendritic growth, b) equiaxed dendritic growth.

Microstrutures in Wrought Steel Products.

A deep understanding of steel microstructures has enabled the steelmaker to exploit systematically the property potentials of the soft iron. A major objective has been to increase strength without giving away too much of toughness, with good weldability retained, and all this at minimum cost. Increasing strength is not a problem, and for this four microstructural mechanisms come into play, i.e. solid solution hardening, particle precipitation, dislocation strengthening and ferrite grain size. The first three can only be utilized to a limited extent due to their adverse effect on toughness. Only the fourth takes care of both strength and toughness as appearing from the Hall-Petch relation where both yield strength, σ_y, and fracture strength, σ_f, are related to the ferrite grain size, *d*, and steel composition, σ_0, σ_0^*:

$$\sigma_y = \sigma_0 + k_2 d^{-\frac{1}{2}} \tag{2}$$

$$\sigma_f = \sigma_0{*} + k_3 d^{-\frac{1}{2}} \tag{3}$$

Although the real picture is more complicated than what appears from these relations, they nevertheless highlight the importance of grain size.

A prominent feature of present steelmaking is the focus on microstructural processes which enable grain size and solid state formation of stable precipiates to be controlled. In carbon steel a range of microstructures is attainable, and hence property combinations, through additions of specific microalloying elements in combination with heat treatment and thermomechanical processing /7/. Fine dispersion of carbide/nitrides inhibits austenite grain growth up to fairly high temperatures. Even more stable particles for this purpose would be oxides , being stable at temperatures up to solidus. An example is the so-called Ti-O steels which are deoxidized with titanium only for forming a fine distribution of submicroscopic titanium rich oxide inclusions /8-10/. Depending on their number density, they can strongly influence the steel transformation behaviour, not only by retarding austenite grain growth, but also by providing favourable sites for delta/acicular ferrite nucleation /11-12/. Such attractive effects of oxides, with contribution to both strength and toughness, are entirely dependent upon the ability to control their particle size and morphology. On the other hand, coarse non-metallic inclusions, oxides and sulphides, are detrimental to toughness and in particular to ductility of structural steels. This is due to the fact that the stresses required for void and brittle fracture initiation, σ_v and σ_b, are inversely proportional to the square root of the particle size, *r*:.

$$\sigma_v = k_4 r^{-\frac{1}{2}} \tag{4}$$

$$\sigma_b = k_5 r^{-\frac{1}{2}} \tag{5}$$

A certain morphology control of these harmful types of inclusions must therefore be exercised through improved deoxidation practice, e.g. aluminium for low oxygen and cleaner steel, and calcium for sulphide shape control for improved through thickness ductility. However, the main approach to the problem of clean steel is the application of various types of secondary refining processes. The production of liquid steel with low oxygen and sulphur contents is becoming quite common practice. Carbon is in a particular position. From being the most important alloying element for steel strength, it is increasingly to be regarded as an impurity element. The lower carbon contents required are obtained through vacuum decarburization where the reaction $C+O \rightarrow CO(g)$ also implies a deoxidation.

Microstructures in Iron Castings.

In the foundry industry iron casting microstructures develop partly during solidification and subsequently during cooling in the austenite and austenite-ferrite regimes. Material properties are strongly related to the mode of graphite precipitation which can be influenced through additions to the melt of nodularizing agents and inoculants. Conditions for heterogeneous nucleation are fundamentally involved in these processes /2,3,13/.

Implications Relevant to Possible Ferroalloy Product Developments.

Property profiles of ferrous materials translated into microstructural requirements contain a common fundamental feature , i.e. nucleation and growth of the various constituents composing the microstructure. Methods for producing fine-grained steels are based upon the principle of inhibiting grain growth by use of pinning particles, whilst graphite morphology and distribution in iron castings are influenced by additions of potent inoculants. This appears to form a scientifically sound base for considering a future contribution of ferroalloys in the developments in ferrous material technology.

THEORETICAL ASPECTS OF HETEROGENEOUS NUCLEATION

In product development the road between a trial and error approach to a well-founded theoretical one is still incompletely mapped and obscure. The complexity of the thermodynamics, kinetics and interfacial phenomena involved prevents a single, comprehensive theory to be formed from which a workable alloy recipe can be deducted. Nevertheless, since iron and steel microstructure control is the present key issue where suitable additions of oxide, sulphide and nitride forming elements to the melt are involved, heterogeneous nucleation appears as an essential theoretical feature.

Interfacial Wetting Conditions.

In general, the effectiveness of individual particles to act as heterogeneous nucleation sites can be evaluated from a balance of interfacial energies. It follows from the definition in Fig.2 that complete wetting is achieved when:

$$\gamma_{SL} \geq \gamma_{ES} + \gamma_{EL} \qquad (6)$$

Under such conditions, the nucleus will readily grow from the liquid on the substrate at essential no undercooling.

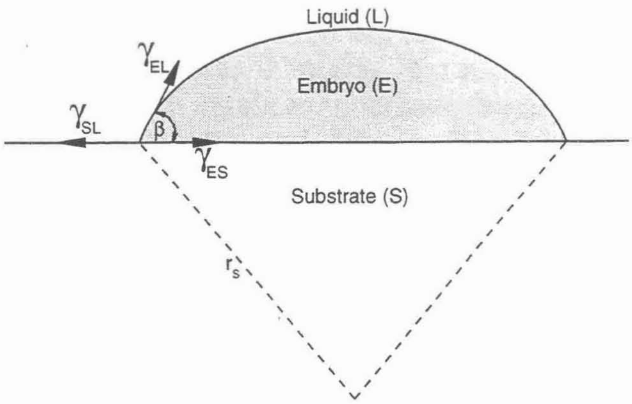

Figure 2. Definition of wetting angle

Catalyst Effects in Heterogeneous Nucleation.

Unfortunately, very little information is available on the substrate/embryo interfacial energy, γ_{ES}. For fully incoherent interfaces, γ_{ES} would be expected to be of the order 0.5-1 Jm^{-2}. However, this value will be greatly reduced if there is epitaxy between the inclusions and the nucleus. The degree of atomic misfit, δ, between the nucleus, *n*, and the substrate, *s*, can be assessed on basis of the Bramfitt planar lattice disregistry model /4/:

$$\delta \frac{(hkl)_s}{(hkl)_n} = \sum_{i=1}^{3} \frac{1}{3} \left(\frac{|(d_{[uvw]_s^i} \cos\theta) - d_{[uvw]_n^i}|}{d_{[uvw]_n^i}} \right) x\ 100\% \qquad (7)$$

where
- $(hkl)_s$ = a low-index plane of the substrate;
- $[uvw]_s$ = a low-index direction in $(hkl)_s$;
- $(hkl)_n$ = a low-index plane in the nucleated solid;
- $[uvw]_n$ = a low-index direction in $(hkl)_n$;
- $d_{[uvw]n}$ = the interatomic spacing along $[uvw]_n$;
- $d_{[uvw]s}$ = the interatomic spacing along $[uvw]_s$;
- θ = the angle between the $[uvw]_s$ and the $[uvw]_n$

The undercooling, which is a measure of the energy barrier to heterogeneous nucleation, has been shown to increase monotonically with increasing values of the planar lattice disregistry /4/. Accordingly, the most potent catalyst particles are those which also provide a good epitaxial fit between the substrate and the embryo.

Case Studies.

The validity of the principles involved in particle-stimulated nucleation is further elaborated in the following two cases.

Ductile cast iron

Whereas nodularization, for instance through a Mg-treatment, is required for graphite spheroidization, inoculation is a way of controlling microstructure by minimizing undercooling and increasing the number of graphite nodules during cast iron solidification. Added to the liquid iron just prior to casting the inoculant provides a suitable phase for the graphite nodule nucleation upon cooling. The most prominent inoculant presently used is ferrosilicon containing small quantities of elements, such as Ca,Al,Zr,Ba,Sr and Ti. The inclusions formed are complex and of a heterogeneous chemical nature. After nodularization both Mg and Ca containing suphides and silicates can form, and with reference to Fig.3(a), the dominating constituent phases are MgS,CaS,$MgO{\cdot}SiO_2$ and $2MgO{\cdot}SiO_2$ /2/.

After inoculation with Ca,Ba or Sr-containing ferrosilicon, hexagonal silicate phases of the $XOAl_2O_32SiO_2$ or the $XOSiO_2$ type form at the surface of inclusion where an exchange reaction with MgO is probably involved, Fig.3(b). The presence of phases of this nature will enhance the nucleating potency of the inclusions with respect to graphite. As illustrated in Fig.4 the (001) basal planes offer particularly favourable sites for graphite nucleation since these facets represent a good match for development of coherent/semi-coherent low energy interfaces between substrate and nucleus. High purity ferrosilicon doesn't show an inoculating effect /2/. This highlight the fundamental importance of the minor elements contained in the alloy, and in search of more efficient inoculants the recognition of nucleation theory as a guiding principle should be duly observed.

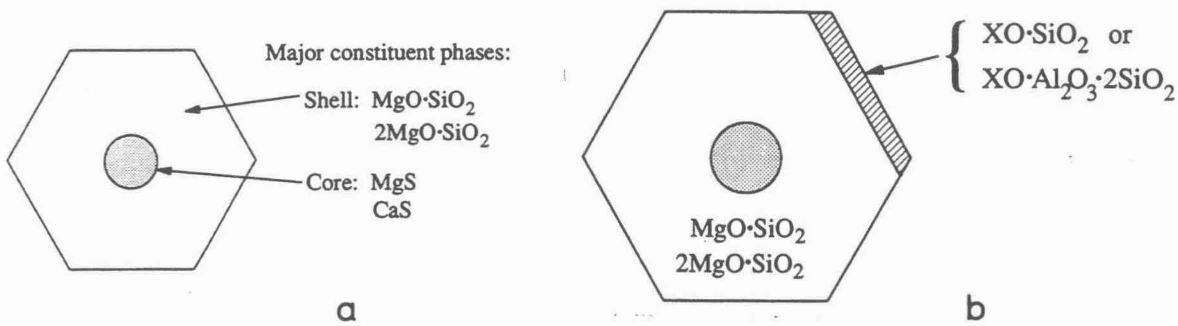

Figure 3. Non-metallic inclusions commonly observed in ductile cast iron; a) Constituent phases present after nodularization with Mg-containing FeSi, b) Phases formed after inoculation with Ca, -Ba or Si containing FeSi. After Skaland et al. /2/.

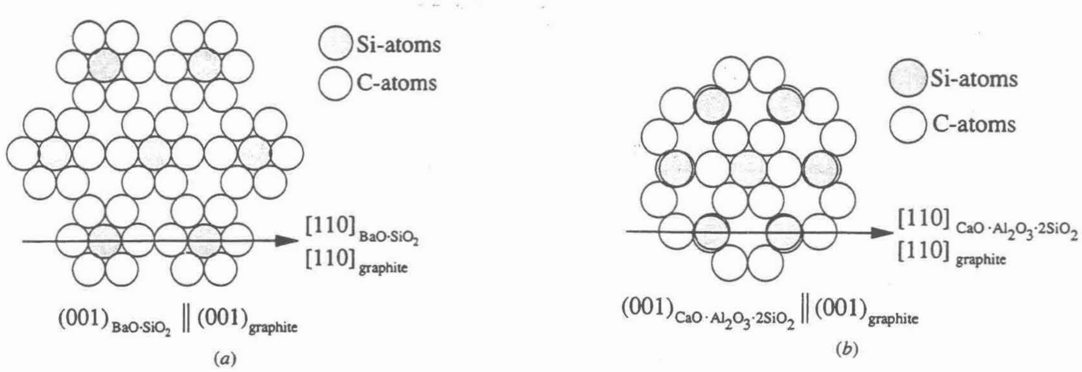

Figure 4. Details of lattice arrangement at nucleus/substrate interface after inoculation: a) Coherent graphite/$BaOSiO_2$ interface, b) Coherent graphite/$CaOAl_2O_32SiO_2$ interface. After Skaland et al. /2/.

Low Alloy Steels.

Inclusions commonly found in steel will, depending on their origin, be either exogenous or indigenous. The first type arises from entrapment of slag, while the indigenous one is formed as a result of deoxidation reactions for oxides or precipitation reactions for nitrides and sulphides. As a result of the complex alloy system involved the latter group is almost always observed to be heterogeneous, i.e. multiphase particles of angular or spherical shapes, and also with different crystallographic characteristics

/14/. An exception may be plain C-Mn steels where the oxide inclusions tend to be predominantely glassy, spherical, manganese silicates.

As previously pointed out, non-metallic inclusions may act as favourable nucleation sites for delta ferrite during steel solidification, and by doing so grain size refinement of as-cast microstructure is promoted /4-6/. According to the data presented in Fig.5, CeS,CaS,RE_2O_3 and TiN are identified as the most potent phases with the ability to facilitate delta ferrite nucleation at low undercooling. Referring to Fig.6(a) and (b), TiN has the NaCl crystal structure while delta ferrite is body-centred cubic.

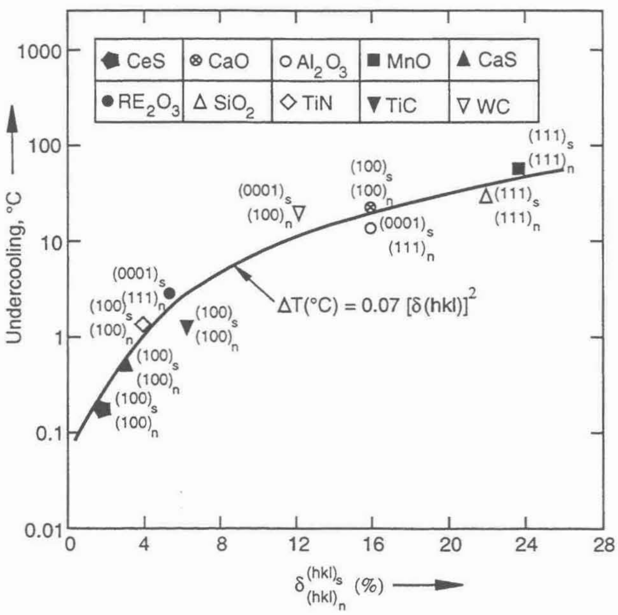

Figure 5. Relationship between planar lattice disregistry and undercooling for different nucleants in low-alloy steel. Data compiled by Grong /1/.

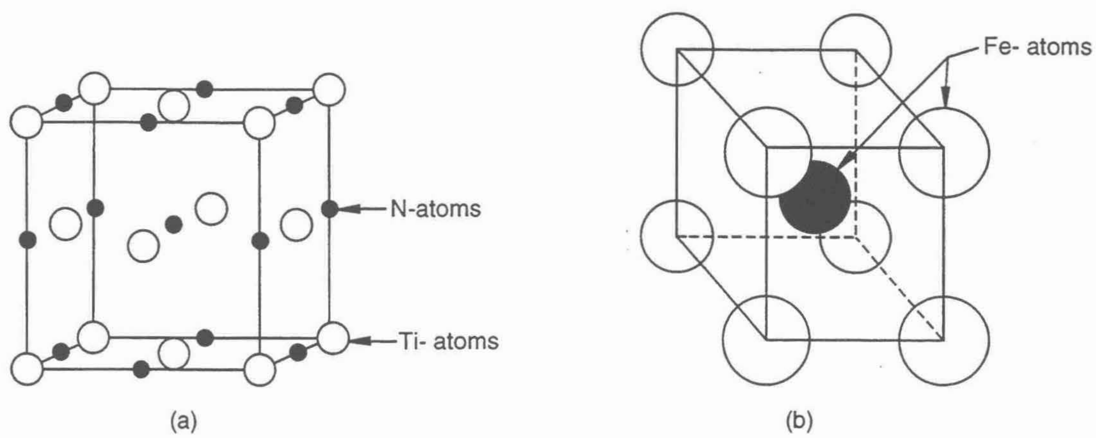

Figure 6. Crystal structures of titanium nitride and delta ferrite (schematic).

According to Fig.7(a) it is obvious that a straight cube-to-cube orientation relationship between TiN and δ-Fe is not compatible with a small lattice disregistry. The matching situation is greatly improved if the two phases are rotated 45° with respect to each other, Fig.7(b), conforming to the following orientation relationship:

$$(100)_{\delta\text{-}Fe} \parallel (100)_{TiN}$$

$$[110]_{\delta\text{-}Fe} \parallel [100]_{TiN}$$

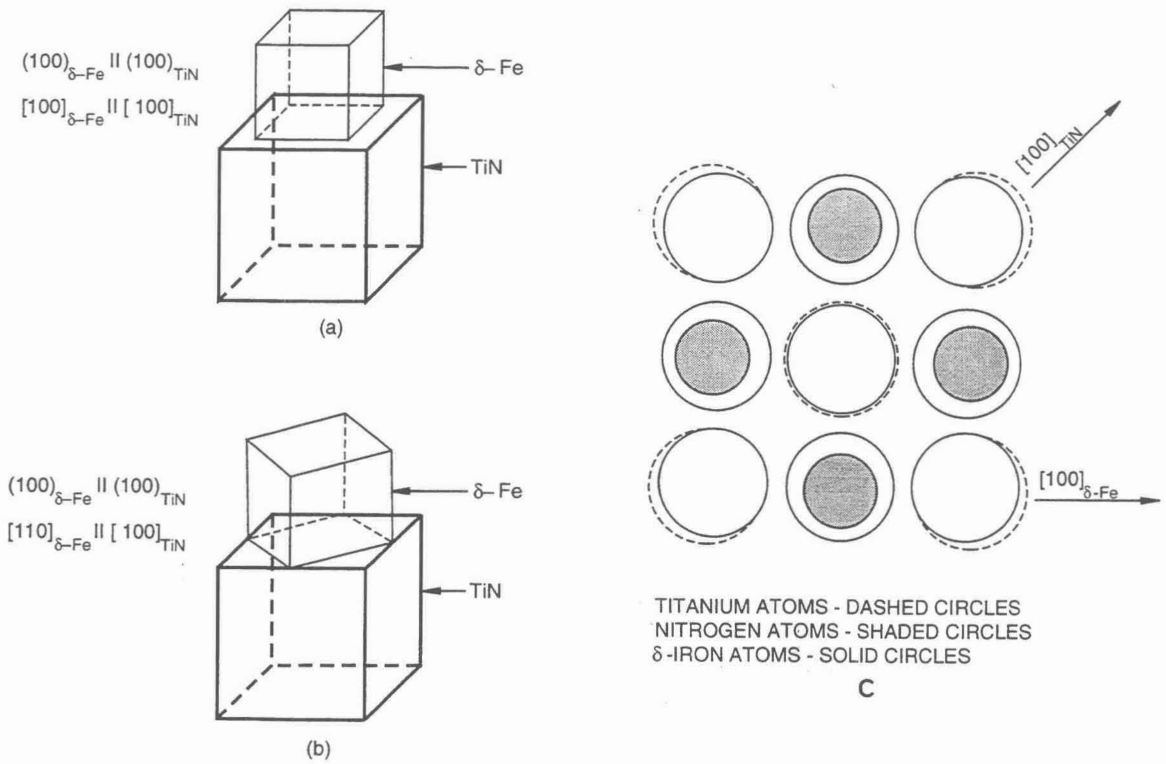

Figure 7. Possible crystallographic relationships between titanium nitride and delta ferrite (schematic); a) Straight cube-to-cube orientation, b) Twisted cube-to-cube orientation, c) Details of lattice arrangement at TiN/delta ferrite interface. After Grong /1/.

The resulting crystallographic relationship at the interface is illustrated in Fig.7(c). Since the lattice arrangements are similar, equation (7) reduces to:

$$\delta^{(100)}_{(100)} = \left[\frac{a_0^{TiN} - \sqrt{2}\,a_0^{\delta\text{-}Fe}}{\sqrt{2}\,a_0^{\delta\text{-}Fe}}\right] 100\% = \left[\frac{0.431 - \sqrt{2}\ 0.293}{\sqrt{2}\ 0.293}\right] 100\% = 4\%$$

where a_0 is the lattice parameter.

Compared with the data in Fig.5 the calculated lattice disregistry conforms to an undercooling of some 1 to 2°C. This is a value sufficiently small to facilitate heterogeneous nucleation of new delta ferrite grains ahead of the advancing interface during solidification.

In literature quite convincing circumstantial evidence is to be found indicating that intragranular nucleation of acicular ferrite is preferentially associated with specific types of non-metallic inclusions, i.e. γ-Al_2O_3, $MnO{\cdot}Al_2O_3$ and TiN due to catalyst effects. The development of a faceted ferrite nucleus which exhibits a rational orientation relationship with both the austenite and the inclusions would require that the substrate and the austenite have similar crystal structures and identical lattice orientation. The catalyst particles must therefore be cubic and bear an orientation relationship with the austenite which lies within the Bain region /1/. Measurements of orientation relationships and interplanar spacings show that the latter condition is satisfied under the prevailing circumstances /15/. The former requirement cannot generally be met because inclusions form in the liquid state prior to the solidification process /1/. Nevertheless, even if the inclusion orientations were perfectly random, theoretical calculations show that about 12 per cent of the inclusions will contain, purely by chance, a cubic phase which lies within the Bain region /1,15/. This intrinsic density of heterogeneous nucleation sites is sufficiently high to promote the formation of fine, interlocking acicular ferrite laths during the $\gamma \rightarrow \alpha$ transformation in the steel. An example of multiple intergranular nucleation of acicular ferrite is presented in Fig.8.

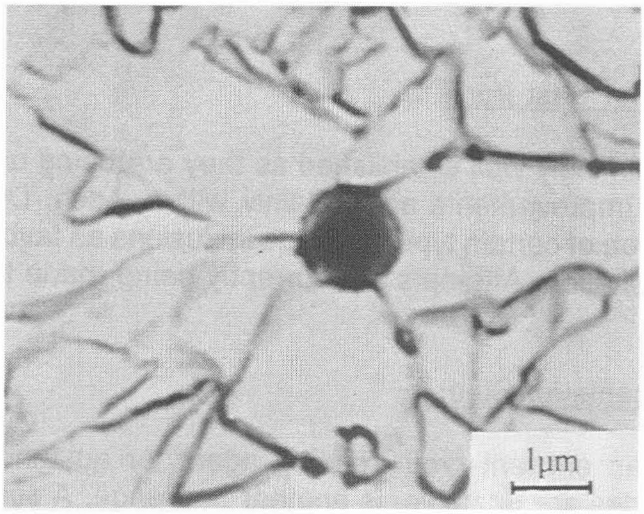

Figure 8. SEM micrograph of a carbon extraction replica showing evidence of multiple nucleation of acicular ferrite at an Al-Ti containing steel inclusion orientated within the Bain region. From Grong /1/.

The cases discussed above demonstrate the fundamental importance of the nucleation aspects of particle/inclusion formation in development of desired microstructures. Although the theory is still incomplete, its main features are generally recognized and substantiated to an extent which makes it serve as a sound basis for further improvement of ferrous material properties.

THE FERROALLOY CONNECTION AND FUTURE CHALLENGES

Ferrous material technology is developing rapidly by implementing in a practical way the fundamental understandings arising from basic research done over the last few decades. The empirical element is quickly fading away, and the established theoretical framework is comprehensive enough for anticipating further progress. In steel refining it is possible to arrive at:

$$\underline{\Sigma}\ \%\underline{C} + \%\underline{N} + \%\underline{O} + \%\underline{P} + \%\underline{S} \approx 0.005\text{-}0.01 \text{ wt\% } (50 - 100 \text{ ppm})$$

and thus providing an excellent base melt for subsequent alloying /16/. On this background the immediate implications to ferroalloys are stricter specifications in respect to higher uniformity, consistency and sizing, and lower impurity element contents.

Guidelines for Alloy Design.

On the other hand, the vital importance of microstructure control in iron and steel manufacture brings about opportunities to the ferroalloy producer in the way of special alloys through which the microalloying elements needed for microstructure developments can be added in a controlled manner at the right time and in the right place during the processing of the ferrous materials. Special attention should be paid to deoxidation where silicon and also manganese not only are acting as carrier for the active micro-alloying elements required, but are also protecting these from being lost through oxidation by taking part in the deoxidation process.

Treatment Alloys for Cast Iron.

Inoculants are seemingly well established as they are being used in grey and ductile iron castings, but improvements are certainly within reach. Due attention should be paid to the formation of certain types of oxide inclusions as favourable nucleation sites for graphite precipitation. Attempts are currently being made to realize these ideas.

Grain Refining Agents for Steel.

Development of an efficient grain refining agent for austenitic cast steel in which carbides and nitrides are unstable, is another challenge. A solution may be found by arranging for a controlled precipitation of oxides and/or sulphides through a late addition. Along the same line, an addition agent which enables ferrite grain refinement by precipitation of a fine dispersion of oxides in the liquid steel is an attractive proposition.

Methods of Addition.

Apart from the necessity of close compositional control are also questions about where and when these additions should be made, e.g. to the ladle, the tundish or to the mould. Bearing the intended function in mind, the application of a cored wire system appears attractive. Another approach is through the powder metallurgy route for making composites, for instance to be used in a plunging operation. Both give considerable latitude for compositional variations and the opportunity for addition to be made in the right place.

Concluding Remarks.

The purpose of this paper has been to present a survey of various aspects of microstructure control as already being practised in ferrous metallurgy and the heterogeneous nucleation mechanisms involved. Further developments will certainly have implications to the ferroalloy industry, and we have tried to demonstrate that the existing theoretical framework is adequate for forming a sound basis for improved products exploitation. It seems timely that the ferroalloy producer take advantage of the accumulated knowledge derived from previous fundamental research within the ferrous sector, as the steelmaker presently is doing in full measure.

REFERENCES

1. Ø.Grong: "Metallurgical modelling of welding"."
   The Institute of Materials, London 1994.

2. T.Skaland, Ø.Grong and T.Grong: Metall.Trans.A, 24A (1993),
   2321 - 2345.

3. T.Skaland, Ø.Grong and T.Grong: Metall.Trans.A, 24A (1993),
   2347 - 2353.

4. B.L.Bramfitt: Metall.Trans. 1 (1970), 1987 - 1995.

5. Y.Nuri, T.Ohashi, T.Hiromoto and O.Kitamura:
   Trans. ISIJ, 22 (1982), 399 - 407.

6. W.G.Wilson,L.J.Heaslip and I.D.Sommerville:
   Journal of Metals, 37 (1985), 36 - 41.

7. R.W.K.Honeycombe:" Steels - microstructure and properties"
   Edward Arnold (Publishers) Ltd., London 1981.

8. F.J.Barbaro, P.Krauklis and K.E.Easterling: Mater.Sci.
   Techn. 5 (1989), 1057 - 1068.

9. H.Homma, S.Ohkita, S.Matsuda and K.Yamamoto:
   Weld.J., 66 (1987), 301s.-309s.

10. Y.T.Pan and J.L.Lee: Proc.3rd. Int.Confr. Trends in Welding Research,
    Gatlinburg (TN), USA, June 1992, pp.539 - 543, Publ.ASM International.

11. T.Gladman: JOM 44 (1992), 21 - 24.

12. T.Gladman: Ironmaking and Steelmaking, 21 (1994), 170 - 173.

13. R.Elliott:" Cast iron technology", Butterworths, London, 1988.

14. R.Kiessling:" Non - metallic inclusions in steel".
    The Metals Society, London 1978.

15. Ø.Grong, A.O.Kluken, H.K.Nylund, A.L.Dons and J.Hjelen:
    " Catalyst effects in heterogeneous nucleation of acicular ferrite",Metall. Trans. A
    (in press).

16. W.Pluschell. Stahl und Eisen, 110 (1990) No.5, 61 - 70.