The electroslag remelting of high-nitrogen steels

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Steels containing nitrogen at levels which are at or above the 1Bar saturation solubility limit in the liquid at the liquidus temperature offer considerable metallurgical property advantages in many respects. For example, when nitrogen is used as a substitute for carbon in stainless grades, the alloys have superior corrosion properties especially in biomedical applications: nitrogen as a strengthening element in tool steels offers advantages in freedom from carbide particles which affect the polishability. Most of the steels grade of interest require electroslag remelting to control segregation without loss of nitrogen and the behaviour of nitrogen during this process is the subject of this work. It is concluded that the required process pressures are closely related to the alloy composition and that to prevent porosity in the product the ESR step must be carried out at an appropriate overpressure of either nitrogen or argon. The addition of nitrogen during ESR is also discussed and it is shown that this is possible only through solid additives.
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1. Introduction

The thermochemistry of nitrogen solutions in steels is very well established through laboratory experimentation, principally using the direct method developed by Sieverts [1–3]. Generally, the saturation solubility of nitrogen closely follows Sieverts' Law as a function of pressure and is a positive function of temperature. The most pertinent features of these properties are that there is a very substantial difference in the solubility around the liquidus temperature depending on whether or not the alloy solidifies as the ferrite or austenite phase. Nitrogen is not very soluble in ferrite but is quite soluble in austenite, to the extent that if the alloy solidifies as the austenite phase, the solubility below the liquidus temperature is an inverse function of temperature, in contrast to the direct function above that temperature. This behaviour is illustrated in Figs 1–3, where we contrast the two different aspects of the solubility function.

The solubility is enhanced by additions of elements which form stable nitrides relative to Fe_3N, such as Ti, V and Cr, but is decreased notably by Si and C. The balance between Cr, C and N is the dominating feature in the formulation of the high-nitrogen stainless grades, where the ultimate aim is to reduce or eliminate the carbide precipitation reactions and at the same time reduce the nickel content without compromising the alloy properties. The reduction in carbide precipitation imparts better corrosion resistance to pitting: the elimination of nickel makes the alloy more suitable for biomedical applications. With respect to the tool steels, primary carbide precipitation is reduced by substitution of nitrogen to the point where no primary carbides are formed, hence considerable enhancing the alloy polishability which is a key factor in the use of these alloys as die materials.

The ESR process is commonly used for these steel grades since almost all of them are required in ingot diameters which produce significant centre segregation if permitted to freeze in a conventional static cast mode. It is feasible to carry out the ESR process under elevated pressure (although the mechanical complications are significant) which introduces the possibility of making alloys which have nitrogen contents exceeding the 1 Bar solubility limits. Pressure melting also provides a means of controlling the development of porosity due to ex-solution of nitrogen during phase change or cooling. Equipment for pressure ESR has demonstrated the practicality of melting at pressures up to 16 Bar [4] in ingot diameters up to 800 mm. The ESR technique itself is not sensitive to pressure and the principal complicating factors are mechanical rather than metallurgical. The main difficulty in the process sequence lies in the decision of how to add the alloying amounts of nitrogen. The most straightforward addition method is by blowing nitrogen into the bath of an electric furnace, or adding a high-nitrogen master alloy such as ferrochromium or ferromanganese or an addition of silicon nitride. If the furnace is operating under atmospheric pressure the maximum nitrogen addition will be the solubility limit at the liquid temperature. The nitrogen will be rejected during cooling and solidification and the usual result is a cast electrode structure which contains a large amount of porosity. Upon subsequent electroslag remelting the porosity will be released as nitrogen gas, some of which
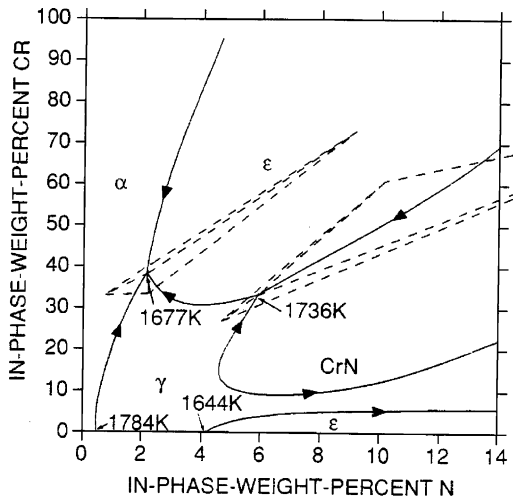
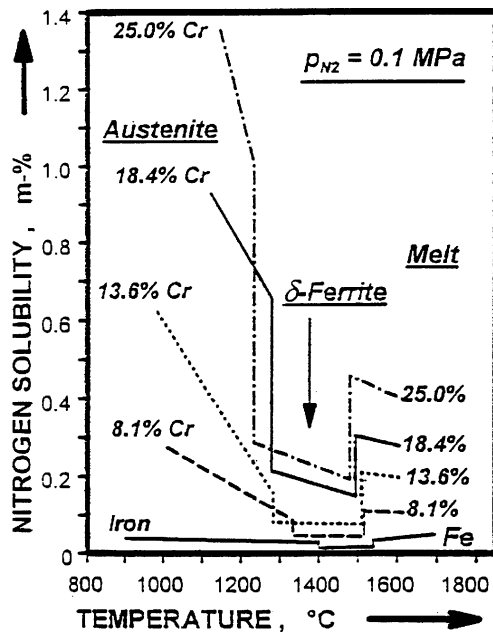*Figure 1* Fe-Cr-N liquidus projection surface.

Figure 2 Nitrogen solubility in binary Fe-Cr alloys.
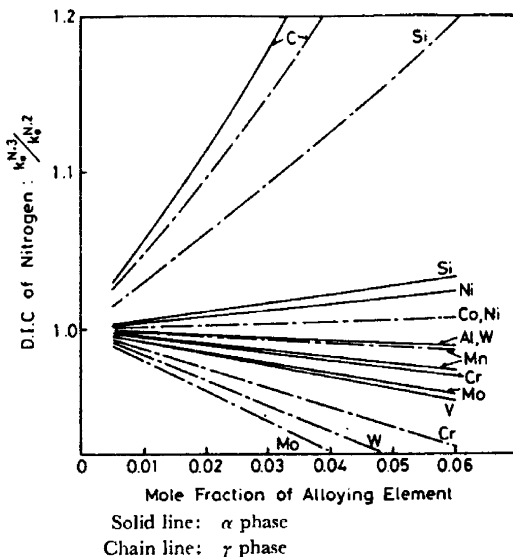

Figure 3 Effect of alloy elements on the solubility of nitrogen in iron.

will go into solution in the alloy at the electrode tip to an extent which depends on the temperature in that region. Since the liquid metal on the electrode tip is not substantially superheated above the liquidus temperature, the nitrogen content of the liquid falling from the electrode is lower than the maximum content in the liquid in the original electric-arc melt, which causes the content of the final ingot to be lower than the addition amount in the electrode. If the ESR melt is carried out under an elevated pressure (of either argon or nitrogen), the nitrogen content of the electrode can be carried into the ingot so producing an ingot which has the same nitrogen content as the electrode. Nitrogen pick-up from the gas phase is negligible since the solubility of nitrogen in a conventional ESR slag is very small. (The small nitrogen loss frequently experienced during ESR of similar steels is probably due to the release of nitrogen gas from electrode porosity).

The above technique will serve as a method for producing alloys in a conventional ESR furnace when the requirement for nitrogen content is significantly below the saturation solubility. It is regularly used in industrial practice for alloys such as tool steels and some ferritic stainless grades where only a small addition of nitrogen is called for in the specifications. Using a pressure ESR larger amounts can be retained, but the limit remains that of the cast electrode. High-strength ferritic steels have been proposed, for example for LBGT applications, in which the nitrogen content is very close to the saturation solubility at the liquidus. In these steels, although the nominal nitrogen content can be retained, unless elevated pressures are used the ingot will contain porosity which cannot be removed by forging. One of the questions to be addressed in this study is that of determining what over-pressure must be applied to prevent the formation of such porosity.

It has been proposed that additions of nitrogen directly to the ESR furnace would circumvent some of the above limitations. In order to add a sufficient quantity of nitrogen without seriously changing the alloy composition with respect to other elements there are few potential additives. Compounds such as calcium nitride which would provide only nitrogen to the alloy are not sufficiently stable to permit handling in an industrial system. High-nitrogen ferroalloys do not contain sufficient nitrogen and iron nitride itself has an unacceptable content of oxygen as normally prepared in bulk. The compound most widely used at present is silicon nitride, available in bulk in a good level of purity at an acceptable cost. However, this addition introduces a significant content of silicon into the alloy and can only be used in small amounts in low silicon alloys such as tool steel grades in the H13 class. The problem of a suitable additive for this type of steel remains at present unsolved.

Studies are reported [5] on pressure induction melting in which nitrogen is introduced into the alloy by prolonged exposure of the liquid to a high pressure of nitrogen gas, up to 50 Bar. The equipment is complex and at present limited to small volumes of liquid. However, if the casting is also made under a slightly higher pressure, the porosity formed by ex-solution of nitrogen

during solidification can be avoided and in this way samples of high-nitrogen steels for experimental work have been prepared.

An alternative technique, proposed by Medovar *et al*. [6], is to use the ionising property of either a plasma or an arc. The exchange rate of nitrogen across a liquid steel surface has been extensively studied with the conclusion that the rate is controlled by the surface combination or dissociation of nitrogen molecules [7]. Since nitrogen is not surface active in liquid steels the rate is strongly reduced by the presence of surfactants such as oxygen and sulphur in amounts down to the ppm level [8]. In conventional melting techniques such as ESR the oxygen activity in steels is sufficiently high that the nitrogen exchange rate is very slow, leading to the need for additions of nitrides directly into the solution rather than additions from gas-phase nitrogen. The presence of a an atomic nitrogen plasma (either from a nitrogen plasma torch or from the plasma region of an arc through nitrogen gas) greatly accelerates the pick-up of nitrogen by eliminating the need for the dissociation step on the surface since atomic nitrogen is absorbed directly into atomic solution in the metal. This situation also leads to equilibrium contents which are higher than those predicted from Sieverts Law. The simplest mechanism for this process is the use of nitrogen blowing in an arc furnace, but plasma torches [9] and the "arc-slag" process [6] have been extensively used for the same purpose. Unfortunately, none of these processes offers the precise solidification control of ESR and although they are potentially useful for the manufacture of steels which are not segregation sensitive, their usefulness in many of the required steel grades appears to be limited. They are, however, processes which could be used for the manufacture of electrodes to be subsequently remelted by ESR. A general review of the melting of high nitrogen steels by various processes is given by Feichtinger [10].

2. Solidification of high nitrogen steels
2.1. Definition of the problem
The example steel class studied in this work is that of the hot-work die steel, "Dievar", which is similar to the general grade H13;

The purpose of nitrogen substitution for carbon in this composition is to reduce the presence of large carbides and also to increase the secondary hardening capability of the alloy. The mechanical property advantages are summarised in "High Nitrogen Steels" [11]. This alloy solidifies initially as ferrite and when the composition of the remaining liquid has been sufficiently changed by segregation austenite precipitates leading to a final solidification of a very small amount of carbide eutectic. Nitrogen is relatively insoluble in the ferrite phase, but is much more soluble in the austenitic phase than it is in the liquid at the liquidus temperature. It follows, therefore, that if we were able to convert the solidification mechanism to one in which a suitably large fraction of the solidification were to austenite, there would be no rejection of nitrogen and no formation of porosity in the solid. The definition of this situation is the objective of this study.
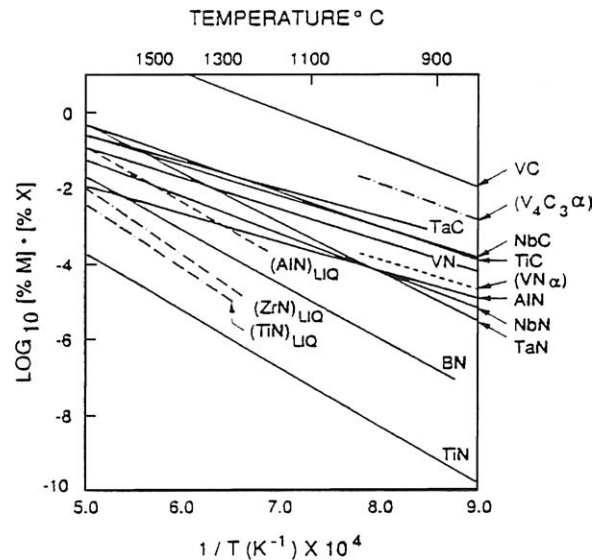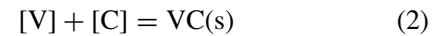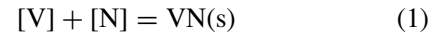

Figure 4 Stability of various nitrides.

2.2. Precipitation reactions
Within the general composition of the tool steels there are two possible precipitation reactions:

$$[V] + [N] = VN(s) \qquad (1)$$

$$[V] + [C] = VC(s) \qquad (2)$$

Data on these reactions as they relate to solubility products is available in the literature [10] and is shown in Fig. 4.

It can be seen from this data that the composition of this steel (Table I) should not precipitate any primary carbide even allowing for the level of microsegregation normally found in large ESR ingots. However, since both V and N segregate strongly in the solidification reaction, it is possible that primary VN could precipitate in compositions with a high level of nitrogen, leading to the presence of undesirable large, hard particles in the final structure.

2.3. Solidification structure
A steel with a composition close to that of the present alloy has been studied previously [13] with the results shown in Fig. 5.

TABLE I Dievar composition

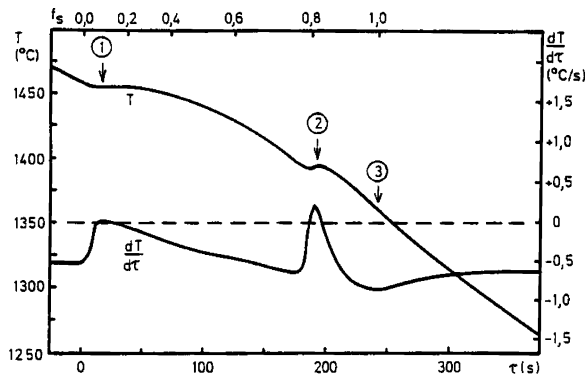| Element	Dievar (wt%)
C	0.36
Si	0.18
Mn	0.50
P	0.006
S	<0.0001
Cr	5.3
Ni	0.05
Mo	2.3
W	0.002
V	0.54
Al	0.001
N	0.03

Figure 5 Solidification of H13 steel at At a rate of 0.5 C/s: (1) onset of ferrite solidification, (2) austenite initiation. and (3) final eutectic.

We can observe the formation of a very small amount of eutectic carbide (due principally to the segregation reaction of carbon) but no formation of primary carbide. The initial solidification is to ferrite at a liquidus temperature of 1470 C, followed by the peritectic reaction to austenite at 1412 C. The austenite primary solidification accounts for approximately 10% of the solidification process. Since the segregation coefficients of V and N are less than unity:

Ferrite precipitation; $\quad k_V = 0.65, \quad k_N = 0.2$

Austenite precipitation; $\quad k_V = 0.4, \quad k_N = 0.5$

it is to be expected that substantial rejection of nitrogen will take place during the formation of the ferrite phase and so either porosity or VN precipitation could arise during this temperature interval. Solidification in the ESR system is quite slow, with solidification times of the order of 1000–4000 s. We would therefore expect that the solidification structures and segregation reactions in an ESR ingot would be close to those predicted by the equilibrium phase diagram. Although the phase diagram for this base composition has not been determined relative to additions of nitrogen, it is possible to obtain a good estimate of the structure and composition changes by using the "Thermocalc" programme. When this is done, we find the results shown in Fig. 6, when it
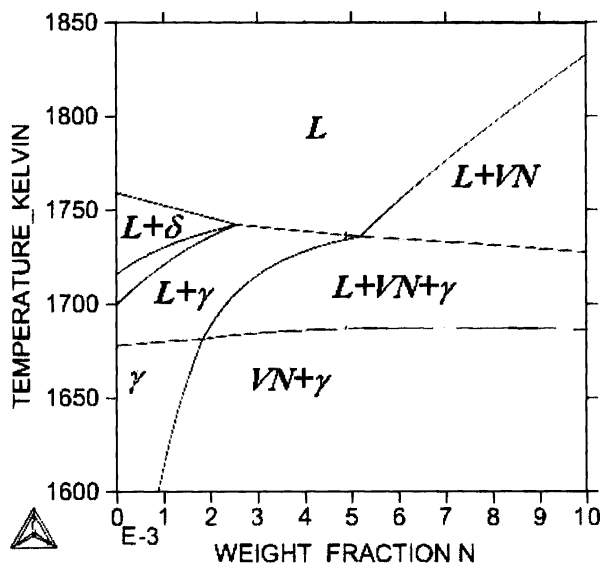

Figure 6 "Thermocalc" equilibrium diagram for the "Dievar" base composition.

is seen that since nitrogen is a strong austenite stabiliser, the precipitation reaction can be converted completely to austenite by a sufficiently large nitrogen addition. As a result such a modified alloy would not develop porosity during solidification under ESR conditions.

3. Experimental programme
3.1. Directional solidification

ESR ingots in the diameter range appropriate to this study (dia < 1000 mm) solidify in a temperature gradient which is a function of radius. However, when combined with the appropriate ingot growth rate, this temperature gradient produces solidification times which are small enough to give columnar-dendritic structures which can be reproduced by the laboratory technique of directional solidification. A typical spectrum of secondary dendrite arm spacings in such an ingot would range from 100 μm at the ingot periphery to 400 μm (a cooling rate of approximately 0.05 C/s in the ingot centre). Typical ESR ingot structures are shown in the literature [14].

Samples of the steel were processed by the method of directional solidification + quenching ("DSQ") in an apparatus shown in Fig. 7. under a gradient of 10 C/mm and a solidification speed of 60 μ/s, giving a cooling rate of 0.6 C/s, which is within the range of cooling
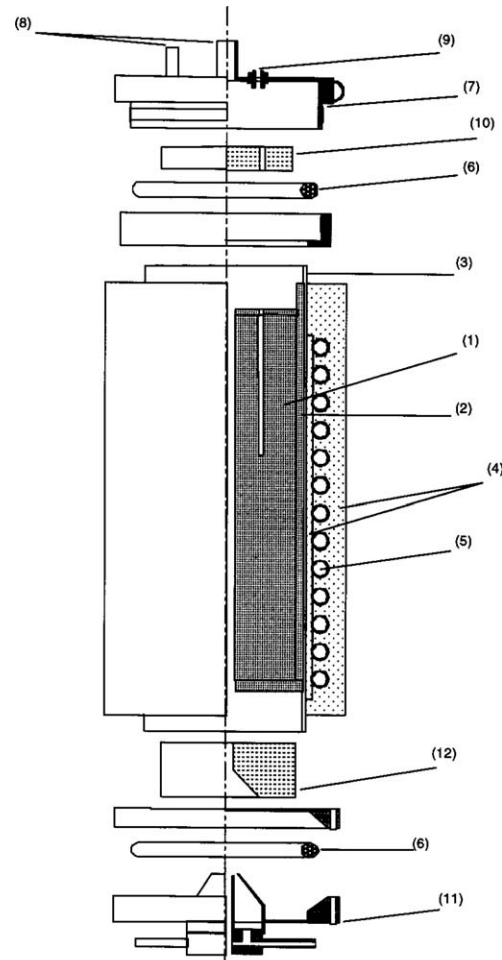

Figure 7 Structure of the DS furnace, showing the graphite susceptor and induction coil arrangement, together with the water-cooled ring and thermal isolation used to establish the required temperature gradient.
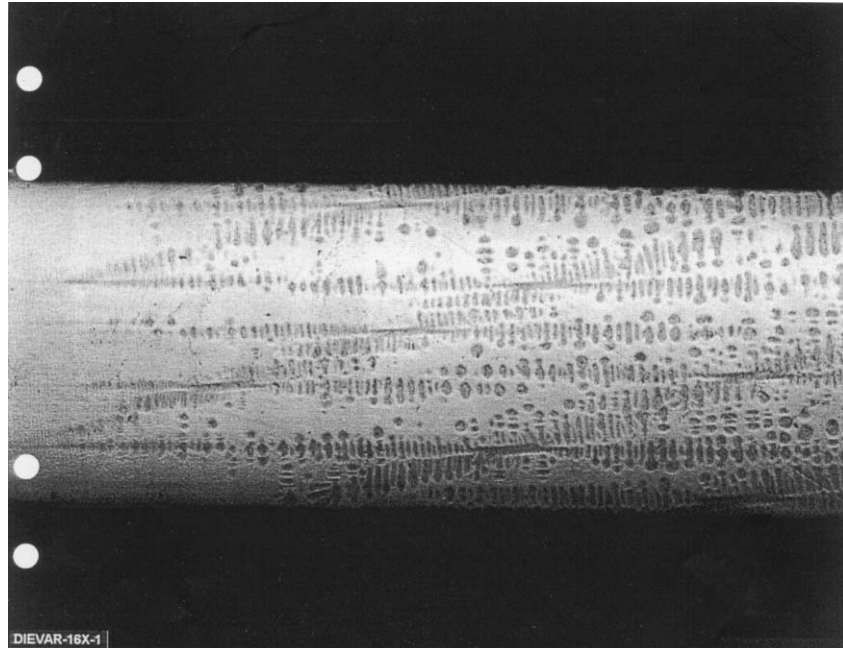
Figure 8 Solidification structure of Dievar.

rates at the periphery of an ESR ingot, but faster than that in a typical ingot centre region.

The sample was quenched when it was partially solid, giving the structure shown in Fig. 8 where the dendrite tips can be seen penetrating into the cooling liquid at the liquidus line.

Since the temperature gradient was previously calibrated, the quenched structure could be correlated with temperature in the axial direction. Several features of the structure are of note. First, the initial solidification produces a dendrite network which is relatively open and it is reasonable to expect (as has been assumed in many models of the ESR process) that there will be a significant mixing between the bulk liquid and the interdendritic liquid, thus reducing the level of segre-

gated elements in the latter in this initial stage. The structure rapidly becomes more dense, as previously found and any mixing must be greatly reduced within 10–20 C below the liquidus temperature. The primary dendrite spacing was approximately 350 μm, as anticipated from previous work [13].

The structure of the alloy solidified under argon is shown in Fig. 9, where it can be seen that almost all of the dendrite structure consists of ferrite, with the final solidification as austenite, followed by a small amount of carbide eutectic.

When the ambient nitrogen pressure is increased to 2 Bar, the additional nitrogen content (0.15 wt%) is not sufficient to produce austenite as the first solid to precipitate, but subsequent segregation converts the
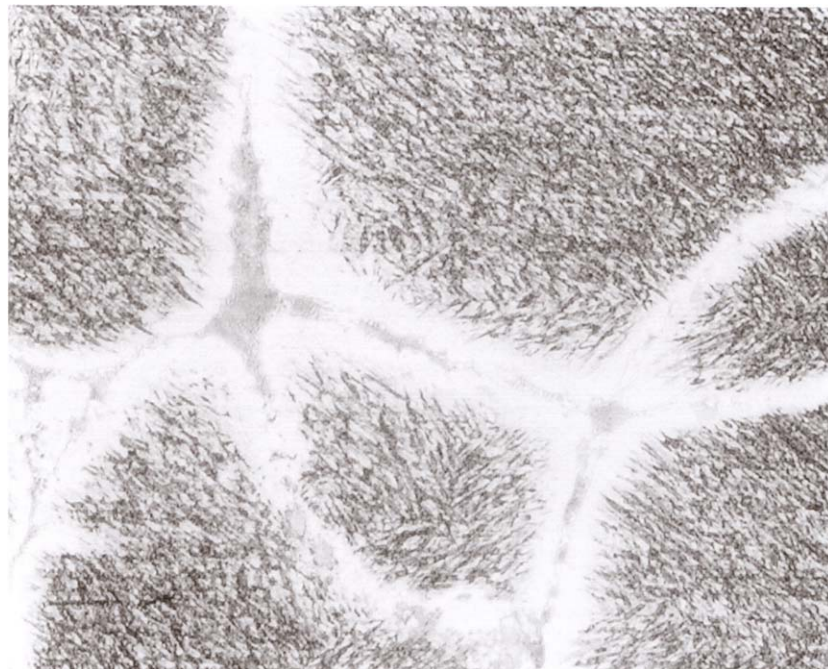

Figure 9 Solidification structure of Dievar, showing austenite and final eutectic precipitation. Solidification time = 1000 s $\times$ 500.
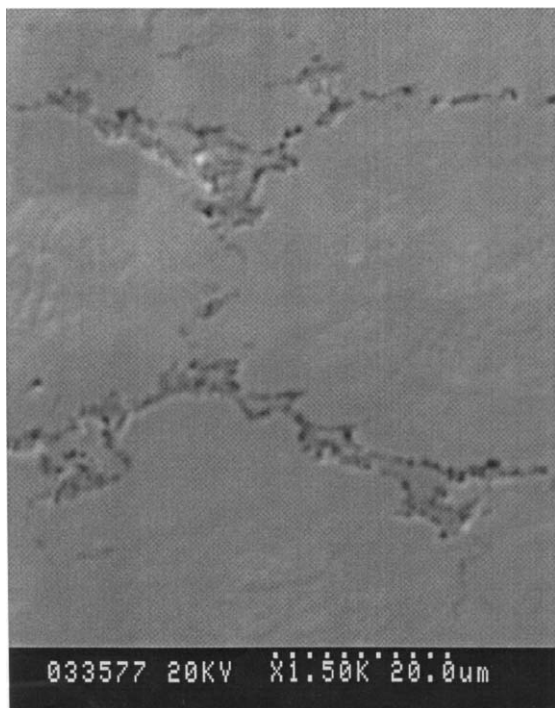
Figure 10 Precipitation of primary VN at the austenite boundary.

precipitation to austenite at a higher liquid fraction than previously observed in argon, but also produces VN precipitates in the final solidification (Figs. 10 and 11).

Under higher pressures, up to 4 Bar, this trend continues until at a nitrogen content of 10 Bar, the initial solidification is to austenite. The nitrogen contents in this alloy composition are at the limits of detection by WDS, and so the segregation coefficient of nitrogen could not be determined directly. However, WDS determination of the vanadium segregation could be carried out and confirms the estimates given above for the ferrite phase.

From the experimental results obtained it can be seen that the addition of nitrogen to the alloy can result in both the primary precipitation of the austenite phase and VN under solidification rates which are at the lower boundary of those experienced in ESR and so might be also expected to produce the same reactions at the slower rates experienced in an ESR ingot centre.

4. Discussion
4.1. Relation to the predicted phase equilibria
4.1.1. 1 Bar nitrogen contents
The computed phase equilibria, derived from "Thermocalc" as shown above, demonstrate that when the nitrogen content of this alloy is low, as normally manufactured (0.05 wt%N), the solidification observed is almost entirely to ferrite, with the austenite phase appearing only at the last stage of solidification at a solid fraction of 0.8 (1417 C), as is reported. [13], corresponding
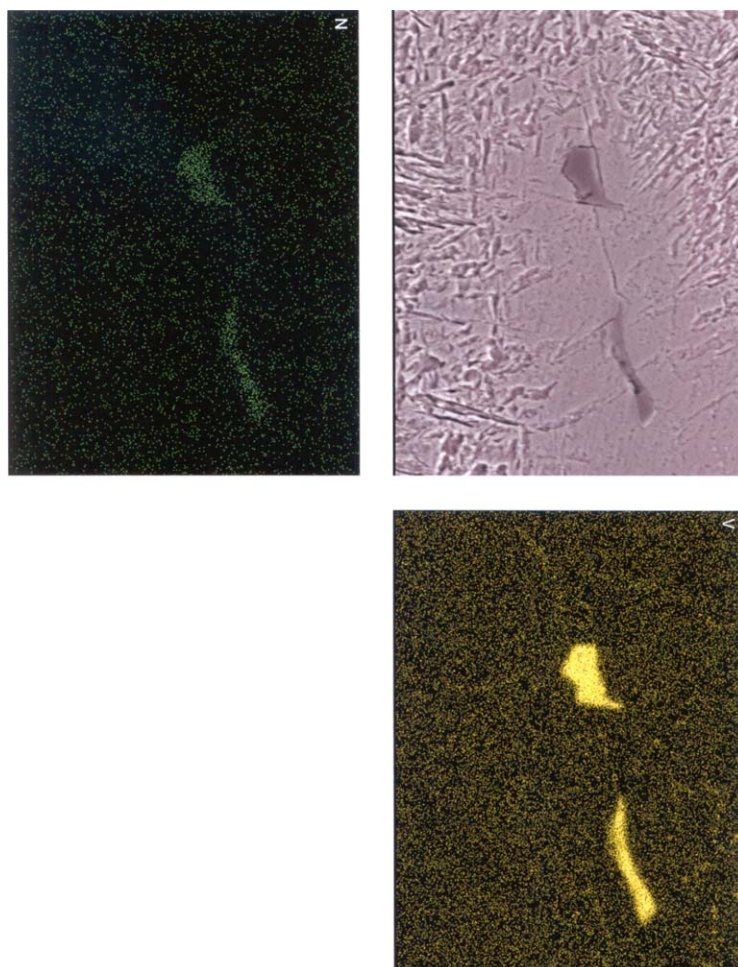

Figure 11 Precipitation of primary VN at 4 Bar nitrogen pressure.

to an undercooling of approximately 5 C. No primary precipitation of VC or VN is seen. When the alloy is deliberately saturated with nitrogen by the addition of CrN at 1 Bar pressure of nitrogen, the nitrogen content rises to 0.08 wt% (as would be predicted from thermochemical considerations of the alloy composition). We observe at this content that although the solidification begins as ferrite, the austenitic phase appears at a much lower solid fraction (approximately 0.4) and we now see small precipitates at the austenite boundaries. The strong rejection of nitrogen from the ferrite phase evidently causes a sufficient concentration increase in the remaining liquid to not only precipitate austenite, but also to cross the boundary of VN precipitation. The primary austenite boundary is reached at 0.2 wt%N, which is in agreement with the ferrite segregation coefficient indicated above at a solid fraction of 0.4, using the Scheil equation. Further segregation into the liquid by N rejection from austenite leads to a final liquid composition of 0.5 wt% N at which point VN is co-precipitated with austenite. If the Lever Rule is assumed, the final liquid concentration of nitrogen would be 0.38 wt%N, at which value VN would not be precipitated. It therefore appears from the experimental finding of VN particles that Scheil conditions are appropriate to this case.

4.1.2. Nitrogen contents > 1 Bar

When the solidification is carried out under a pressure of 4 Bar nitrogen, the liquid composition at the liquidus rises to 0.2 wt%N. The primary precipitation is ferrite, but the additional amount of nitrogen in solution leads to a much greater precipitation of VN as the austenite phase forms. Additional pressure, to approximately 10 Bar would convert the primary solidification to austenite, but at the consequent value of nitrogen content, there would be a rapid onset of VN precipitation with falling temperature, leading to extensive, large primary VN particles in the structure. Previous workers [10] have indicated that with higher pressures the segregation coefficient of nitrogen in the austenite phase rises above unity in which case, therefore, the precipitation of VN should not occur. The work, however, was carried out on 18Mn18Cr steels which may not have the same response to nitrogen pressure as in the present case.

4.1.3. Porosity formation

If a liquid which is in equilibrium with a given nitrogen pressure starts to solidify as ferrite and therefore rejects nitrogen into the remaining liquid, the liquid becomes supersaturated with nitrogen with respect to the ambient pressure and should form gaseous nitrogen to be released from the condensed system, i.e., bubbles should be formed in the interdendritic region, leading to porosity.in the final solid. The question of how porosity forms in a solidifying alloy has been studied by many workers. The context of the studies varies depending on the form of the casting process and on the alloy concerned. Porosity may form due to solidification shrinkage, gas generation or fluid flow, but in the present case

porosity is probably the result of a combination of the first and second of these effects since we do not usually observe extensive macrosegregation defects caused by fluid flow in the solidifying region of the ESR ingot. The pore process consists of a two step reaction:

(a) nucleation of the pore
(b) growth of the pore

Considering the first of these steps, a pore may be nucleated homogeneously in a liquid when the pressure created by ex-solution of gas is greater than the new pore's surface energy:

$$P > 2\sigma/r$$

where P is the gas pressure, σ is the liquid/gas interfacial energy and r is the radius of the nucleated pore. Since the interfacial energy of steel/gas interfaces is quite high, the pressure required to nucleate a pore usually exceeds the available gas pressure in 'real' systems and so homogenous nucleation is not considered to be the normal way to generate new pores. Instead, pores are considered to nucleate on second-phase particles, principally non-metallic inclusions, which have a size range of 'r' such that the required pressure is within that available from the gas ex-solution reaction. Inserting appropriate values of P and σ in the above equation leads to a value of approximately 10 microns for r when the pressure of gas would be equal to that generated when the solution is supersaturated in nitrogen by a factor of 2x. The implication is that we could prevent gas porosity formation in a typical industrial alloy if the nitrogen content at all stages in the solidification were to be restricted to a level below the 2x supersaturation. Some support for this view is to be found in the literature. Arola *et al*. [15] where castings of stainless steels at high nitrogen content were analysed for porosity and the findings related to the presence of alumina inclusions. Castings with many small alumina inclusions formed many micropores, whilst those with low alumina content formed a smaller number of large pores. The porosity was seen to be associated with alumina particles. Since the effect is related to interfacial tension between the particles and the liquid metal, it is also reasonable to assume that features which affect the value of this parameter would also affect the pore nucleation process. It has been suggested [16, 17] that pore size and incidence could be changed by changing the chemical composition of the inclusions and also by making additions of elements to the alloy which reduce the parameter value, such as S, Se and Te [16, 17]. Most studies on pore formation have assumed, probably correctly, that in the alloys of interest there will always be nucleating particles present, and therefore the item of most interest lies in the growth of the pores, rather than in the nucleation process itself. The pore growth mechanism has been related to dendrite growth during freezing by several workers. Svensson [18] developed a model in which the diffusional transport of the gas to the pore site was balanced against the freezing rate to produce a pore-size distribution which could be tested

experimentally. Agreement was found between the predictions and results in the cases of hydrogen and nitrogen porosity formation in steel castings solidified over a range of rates, although in this case the freezing rates were somewhat faster than those found in ESR ingots.

More recently, Rachev [19] has analysed the pore formation process in terms of freezing rate, in nitrogen alloyed tool steels by means of a heat-flow analysis of a conventional casting. The freezing rates were computed from a 2-D finite element model of the cast slab and the porosity analysed microscopically. The maximum primary dendrite spacing observed was 220 microns (as opposed to a typical ESR range of 400–800 microns), the solidification speed was 0.35 mm/s and the temperature gradient may be estimated from the published diagrams to be approximately 16 C/mm. Although these conditions are not the precisely the same as for either DS or a remelted ingot, the data is nonetheless of interest. The pore size under these conditions had an average value of 0.2 mm, i.e., the same as the primary dendrite spacing, and the total porosity was approximately 3%. The model used is more complex than the diffusional balance considered in [18] since it also takes into account the effect of the pressure reduction due to shrinkage and the modification of this pressure by interdendritic fluid flow. An extension of this general model concept has been presented by Atwood [20]: for the porosity formed by hydrogen evolution during the freezing of aluminium alloys. In this model, the cellular automata technique is used to simulate crystal growth, rather than using the assumptions necessary in a finite element model. The process includes fluid movement, diffusional processes and gas supersaturation and provides a realistic description of the growth process when using a random distribution of nucleating sites of approximately 5 microns in radius, which defines the critical supersaturation necessary to initiate the pore. The model is not directly applicable to the present case since it refers in this form to equiaxial solidification, but illustrates the validity of the concept that a realistic nucleating particle size distribution can accommodate all of the gas evolution likely during solidification.

4.1.4. ESR processing

The relation of the above ideas to the present case of porosity formation in the ESR structure is not direct. In the case of nucleation, although the ESR material is likely to be very clean, there is almost certainly a significant concentration of oxide inclusion particles greater than 10 microns in diameter present in the solidifying region. It is reasonable, therefore, to consider that the nucleation process will be that of gas diffusing to the oxide particle and there forming the pore. Once the pore has been nucleated, depending on its size the nitrogen which it contains may not be re-dissolved on subsequent working and heat-treatment, thereby not only removing it from the alloy's metallurgical properties, but also creating the potential hazard of crack nucleation in the product. If the porosity is dispersed and small, from many nucleation sites, it will be removable by forging in the same way as is the typical shrinkage

microporosity present in most as-cast structures. If the alloy is extremely clean and has few nucleation sites, the porosity will be infrequent, but large. It is also possible to conceive of a situation where the growth rate of the solidification front is equal to the growth rate of the pore by gas diffusion and evolution so that the pore will become elongated in the dendrite growth direction. Such elongated, large pores are observed in the case of hydrogen evolution from ESR ingots when the slag used has been unusually wet. They are cylindrical with a diameter comparable with one to four primary dendrite spacings and a length which may be several cm in the growth direction. In such cases, growth marks on the pore surface may be observed which correspond to the movement of the bubble of gas creating the pore. Eventually either the pore grows to a diameter which is unstable and the gas bubble detaches from the solidifying surface; or the incoming metal feed becomes lower in gas content and the feeding of the pore is stopped. Pores of this type have also been produced in experimental DS structures [15] at growth rates which approximately twice those of the ESR ingots. They have also been shown to be responsible for some of the "freckle" defect in certain types of high carbon steels [21]. In the present context, the supersaturation of nitrogen is relatively small and the nucleation process must be considered in relation to the progressive rejection of nitrogen into the liquid as the ferrite phase forms and ultimately as VN is precipitated.

It appears that in this range of steel compositions, increasing the nitrogen pressure in order to place more nitrogen in the solid increases the risk of porosity through the accumulation of nitrogen in the residual interdendritic liquid during ferrite precipitation. When the solidification phase changes to austenite, this problem is greatly reduced, but a limit on the nitrogen content is set even in this circumstance by the formation of primary VN. From "Thermocalc" considerations it does not appear feasible to convert the solidification entirely to austenite by the application of excess pressure to the ESR furnace since the necessary pressure is unrealistically high. It is therefore desirable to change the steel composition to one in which the onset of primary nitride precipitation is suppressed, but in which the solubility of nitrogen is such that a moderate pressure in ESR can produce the contents required for secondary hardening. The requirements for such a composition change would be that the element substituting for vanadium should not be a strong nitride former and not strongly stabilise the primary ferrite phase. If this change is made, from the above considerations it appears that a pressure of no more than 2-3 Bar would be required to maintain the necessary nitrogen content The pressure could be applied as either argon or nitrogen, since the transfer of nitrogen to or from the gas phase in ESR is small unless a large amount of either aluminium or calcium is added to the slag during melting. (This type of addition is not normally used in this range of steels due to its tendency to promote the formation of large oxide inclusions). Nitrogen itself is relatively insoluble in ESR slags. The solubility at 1 Bar is in the range of 0.02–0.04 wt% at the liquidus temperature depending

on the CaF$_2$, CaO and Al$_2$O$_3$ contents [7, 22]. The nitrogen activity, however, is greatly increased when the carbon potential is high, due to the formation of the CN$^-$ ion rather than N$_3$. The necessary carbon potential for this reaction to occur is much higher than that encountered in steel remelting, requiring effectively carbon saturation of the metal/slag system. The problem of nitrogen addition to the electrode or ESR process in quantities exceeding the 1 Bar saturation solubility in the liquid remains to be defined, but ideally would be made using a low silicon, high nitrogen chromium or iron material with low oxygen content.

5. Conclusions

We may conclude from the above study that two phase or peritectic solidification in ESR ingots is under conditions which are close to the thermodynamic equilibrium and may be determined by directional solidification experiments or by using existing thermochemical models of solidification. The peritectic, vanadium- and nitrogen-containing tool steels studied have a optimum nitrogen content of approximately 0.1 wt% N, corresponding to a pressure of 1.4 Bar for saturation of nitrogen in the liquid phase. Segregation then produces only a small amount of VN primary phase as small particles but leaves sufficient nitrogen in solution for the required hardening reactions. Changing the composition of the steel as indicated above shows promise for increasing the nitrogen-driven hardening characteristics without the need for excessive pressures in either the preparation of the electrode or in the ESR process itself.

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