Nitrogen in Superalloys

Alec Mitchell

Advanced Materials and Process Engineering Laboratories
University of British Columbia
Vancouver BC, Canada
e-mail: alecm@interchange.ubc.ca

(Received August 27, 2004)

ABSTRACT

Nitrogen has a significant effect on superalloy mechanical properties, almost without exception in a negative sense. All of the alloys contain strong nitride formers (Ti, V, Nb, Hf, Ta) and will, because of the nitride-former concentration, produce nitride precipitates not only during solidification but also when the alloy is fully liquid and significantly superheated. In this review we present an examination of the problems involved in removing nitrogen from the alloys and also of the mechanisms by which nitrides influence mechanical behaviour. It is concluded that one of the most effective means of control of the nitrogen content lies in the choice of raw materials for the alloy make-up, but that the subsequent nitride formation can be minimised by correct choice of process routes in VIM, ESR, VAR and EBCHM.

1. INTRODUCTION

The root of the nitrogen problem in the superalloys stems from the insolubility of nitrogen in the alloy primary gamma phase, corresponding to the low solubility of nitrogen in solid nickel. Even the addition of relatively large amounts of chromium in the alloy formulation does not significantly change this situation. As simple computations of the complex thermochemistry in the alloys show, the nitrogen content in the liquid is likely to be entirely precipitated as nitride by the end of solidification /1,2/. The nitrogen content of a superalloy seldom exceeds 100ppm, and the dynamic properties are thus largely controlled by the direct influence of the carbide and intermetallic precipitates rather than by nitrides. However, since the nitrides are isomorphous with carbides and with the alloy primary phase, they have a substantial indirect influence on the alloy behaviour. In addition, since the nitride particles are present in the liquid they play a significant role in the agglomeration of inclusions to form defects which are in the size range affecting alloy properties even though the individual particle size range may be below that required for example to nucleate a crack under fatigue loading conditions.

2. MECHANICAL BEHAVIOUR OF THE ALLOYS

The superalloys have been extensively studied in respect to the form and size of defects which influence the dynamic properties /3/. It has been found that the defect size which causes rapid crack growth depends on the alloy strength level but is generally in the size range of 50 – 250 microns. The distribution of individual inclusion particles in the alloys is generally well below this threshold, but agglomeration of both non-metallic inclusions and carbides can readily produce a defect volume with a dimension exceeding this limit. As a result, alloy properties generally show a dependence on inclusion content at high inclusion levels, changing to a dependence on carbide distribution as the oxide inclusion content decreases, since the carbide particles also can agglomerate during precipitation. When there is no carbide agglomeration and no inclusion content the alloy properties are determined by the grain size and the crack initiation points are grain boundaries. An alloy in this latter category could be termed a "superclean" alloy and has the very significant advantage that we can predict its properties solely on a microscopic determination of the grain size. Typical presently-available 'clean' forging-grade superalloys fall into the category where the crack nucleation sites are divided equally between non-metallic inclusions and carbide agglomerations, with specially prepared alloys falling into the category of 100% carbide agglomeration nucleation. In both of these categories, nitride contents play an important role in the agglomeration process.

3. THERMOCHEMICAL CONSIDERATIONS

Since the alloys all contain Ti, it is reasonable to regard the nitrogen thermochemistry as a pseudo-binary problem of the solubility of TiN in the alloy composition. Methods of computational thermochemistry have been applied to the problem and show that the solubility of this compound, as expected, is quite low and also is temperature dependent. A very similar situation has been studied also in the iron-base alloys, where the requisite thermochemical database is more extensive, and the same effects have been found /4,5/. An example of the TiN solubility in an iron-nickel-chromium alloy is shown in Fig. 1. For an example superalloy, IN718, the solubility has been computed /6,7/ and is shown in Figs. 2 - 4 and also in Table 1. Fig. 4(a) shows the solubility of TiN in IN100 illustrating the effect of increased Ti content. It can be

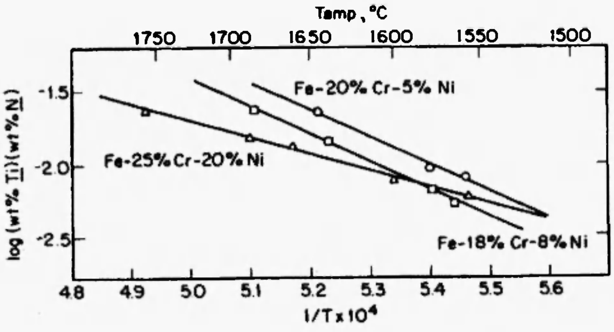


Fig. 1: Solubility of TiN in Fe-Cr-Ni alloys.

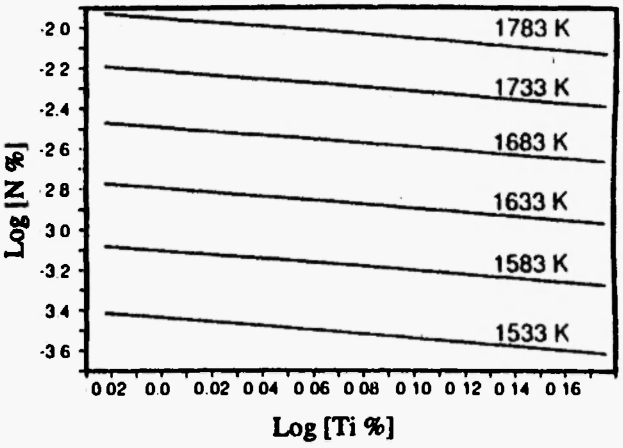


Fig. 2: Temperature and composition dependence of the saturation solubility of TiN in IN718.

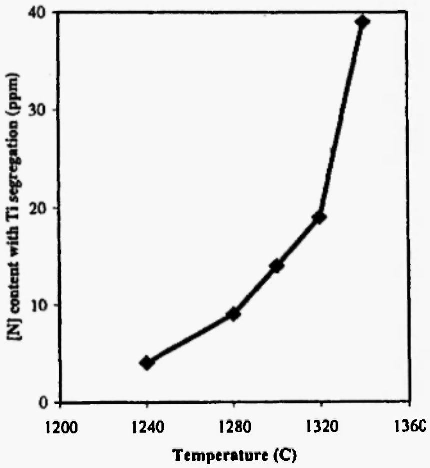


Fig. 3: Temperature dependence of the saturation solubility of TiN during the solidification of IN718, taking into account the segregation of Ti into the interdendritic liquid.

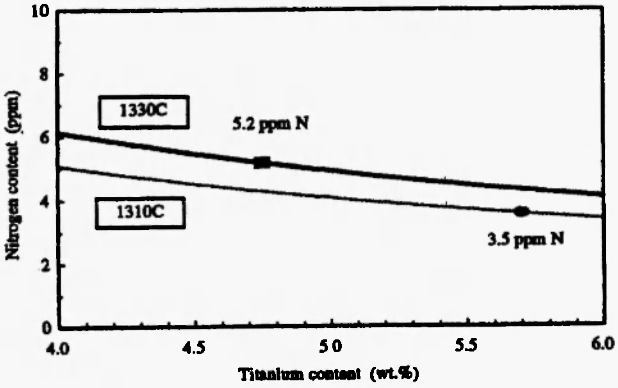


Fig. 4: TiN solubility limit as a function of Ti content in IN100, allowing for segregation on solidification.

Table 1
Saturation Solubility of TiN in IN718

Temperature (K)	PN2 Bar	Saturation [N], ppm
1603	8.9E-6	29
1700	4.8E-5	39
1800	4.0E-4	112
1900	2.7E-3	290
2000	1.2E-2	620

seen that the solubility decreases very sharply through the liquidus temperature (through not only the direct effect of temperature, but also the effect of Ti segregation to the liquid during the formation of the primary solid phase as is illustrated for the case of IN100 in Fig. 5) and notably is in the range of generally specified nitrogen contents in the alloy. The equilibrium partial pressures of nitrogen in the reaction have also been computed for a range of superalloys, showing the expected effect of an increased Ti content. It is to be noted that the equilibrium partial pressures are of the same order as the generally-used industrial vacuum melting equipment. We can expect therefore that in an industrial composition, a substantial part of the nitrogen content will be precipitated as particles in the liquid immediately ahead of the solidifying interface, as shown in Fig. 6, where it can be seen that the size of the primary TiN particles remains essentially constant throughout the solidification process and is the same as that in the liquid at a temperature immediately above that of the liquidus. The remaining nitrogen is precipitated during cooling so that the residual amount in solution at the solidus is very small. Studies have been conducted /6/ to determine if the nitrides will escape from the solidifying interface, since they have a density which is approximately half that of the bulk liquid. It was found that at a solidification rate appropriate to that of an ESR or VAR ingot growth rate, no nitride particles were observed to float from the interface. The nitrogen content remained unchanged through the solidification process. It is to be concluded that even if the particles were able to move within the dendrite network, their solution rate is sufficiently high that extensive re-solution would take place in the temperature gradient of the solidification regime as they rose into the bulk liquid, creating a cycle of solution/precipitation which would lead to a zero net change in the nitrogen content of the system.

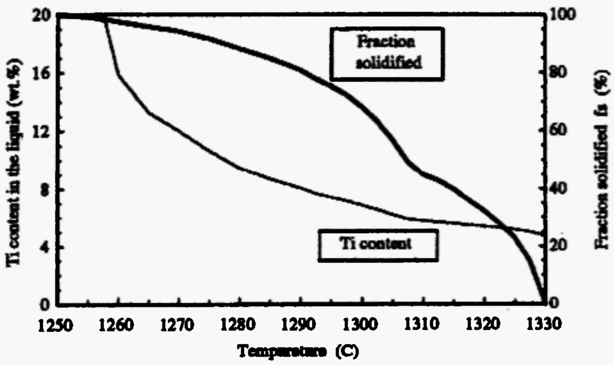


Fig. 5: Ti segregation during the freezing of IN100.

Carbides precipitate isomorphously on the nitride particles at the same time as nitride is also precipitating and the process gives rise to complex 'carbonitrides' in which the structure is layered in a manner reflecting the changing activities of carbon and nitrogen during the freezing process (Figs. 7 & 8). The carbide precipitation process in the solidifying region is strongly influenced by the presence or absence of the nitride nucleant /7/. In the complete absence of nitride particles, primary carbide nucleation in IN718 of low carbon content (<0.02wt%) is entirely suppressed leading to a substantially modified eutectic structure and a changed Laves phase composition /8/. A further effect of carbide nucleation has been noted /9/ in which the TiN/carbide nucleation process in the casting alloys IN713 and IN100 was shown to have a substantial influence on the castability of the alloy. The effect arises through TiN causing equilibrium nucleation of carbides, which then block interdendritic flow and cause the development of microporosity and increase the effective viscosity of the freezing liquid. In the absence of TiN (brought about by EBCHM processing of the alloy to low nitrogen levels), these two effects are eliminated and the reject levels of the alloy castings strongly reduced. (It is to be noted that a similar mechanism has been found for the suppression of freckling in SX alloys).

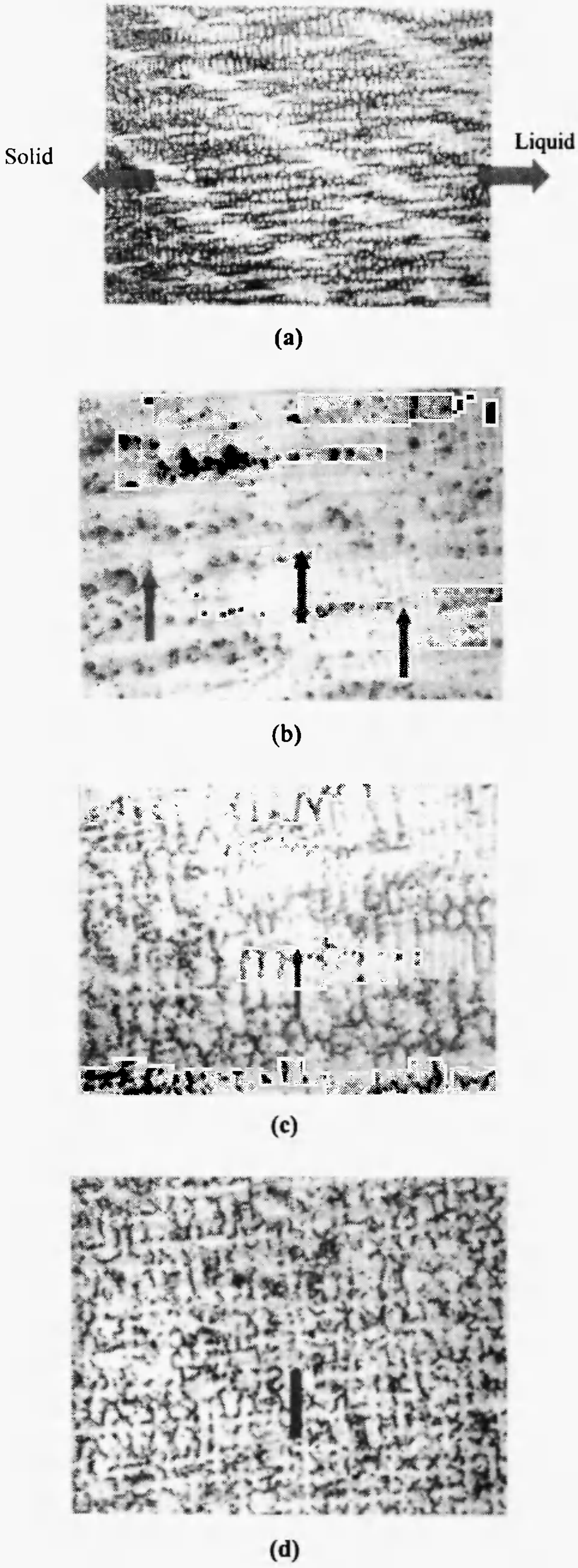


Fig. 6: (a) Liquid+solid region of IN718 in the directional solidification+quenched mode. (x50). (b) Fully-liquid zone of IN718 in the directional solidification+quenched mode. Arrow indicates primary TiN particle (X400). (c) Liquid+solid zone of IN718 in the directional solidification+quenched mode. Arrow indicates primary TiN particle (X400). (d) Full-solid region of IN718 in the directional solidification+quenched mode. Arrow indicates primary TiN particle (X400).

continued...

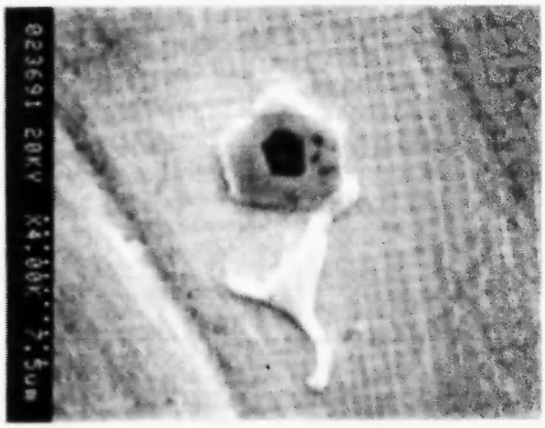


Fig. 7: Primary carbide particle nucleated on a TiN particle.

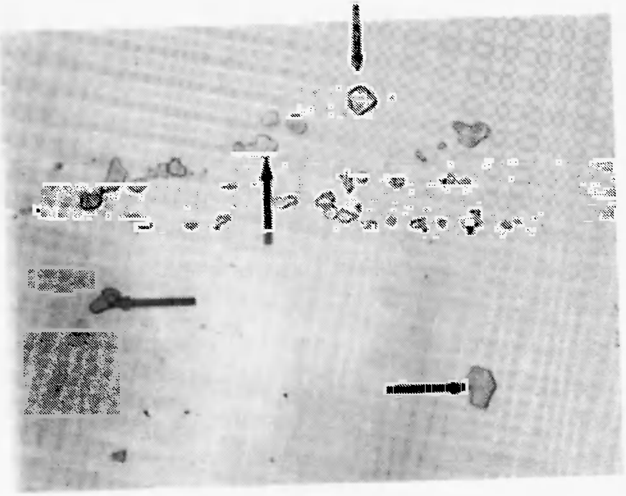
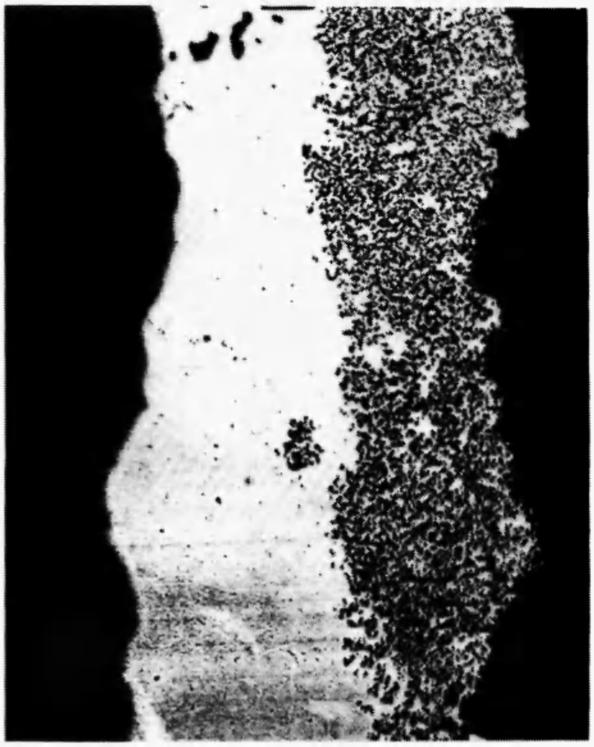


Fig. 8: Large primary carbides nucleated on nitrides.

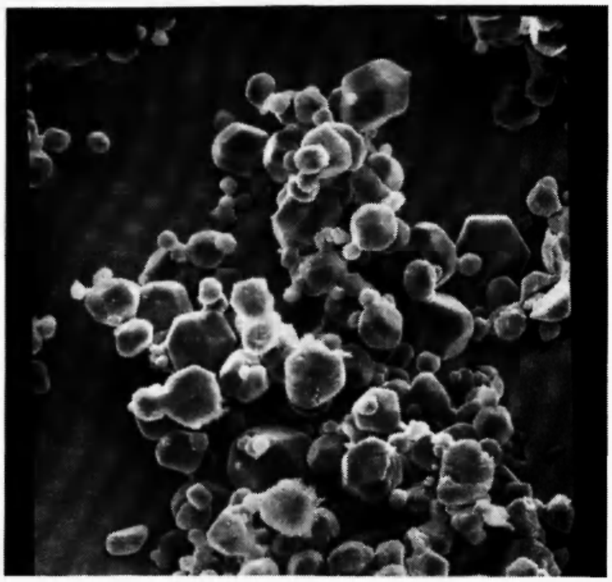
4. NITRIDE PRECIPITATION IN THE LIQUID

Unless the superalloy has been specially formulated, the nitrogen content in the liquid will be at a level where TiN precipitates are present at the liquidus temperature. In the vacuum induction furnace the superheat applied for refining is sufficient to prevent the precipitation of these particles, but as the liquid cools during the casting process precipitation takes place. The particles may then agglomerate with themselves and also with any oxide particles which are present, such as alumina, spinels or magnesia arising from deoxidation or refractory wear. Some of these particles may be removed by the application of filtering techniques, since TiN will adhere to a zirconia surface, but the same adhering mechanism also produces agglomeration in the pouring nozzle (Figs. 9 and 10). Since the pouring stream is seldom stable, the agglomerate can be broken away at intervals to place agglomerated inclusions in the product casting. Subsequent remelting of this product by ESR or VAR does not necessarily decompose or remove the

Fig. 9: Inclusion agglomeration in the VIM casting nozzle (x10) .



(a)



(b)

Fig. 10: (a) Inclusion agglomeration in the VIM casting nozzle (x50) and (b) agglomeration of oxide and nitride inclusion on the surface of VIM refractory nozzle during the pouring of IN718, N=70 ppm.

agglomeration. This mechanism is responsible for a significant fraction of the larger inclusion agglomerates found as crack nucleation sites in the alloy. The most obvious method for avoiding the above problem is to prevent nitride precipitation in the liquid at the superheat temperature used for the casting process, as illustrated in Fig. 11. The thermochemical requirement for this condition can be computed and leads to the conclusion that very low nitrogen levels are needed for this mechanism. In the example alloy IN718, with 1 wt% Ti, the required level is 29 ppm, which is reasonable provided that the alloy can be made with suitably low nitrogen raw materials. However, in the casting alloys, the nitrogen requirement is much lower since the Ti levels are higher. The equivalent value for CMSX4 is 4ppm, which is considerable less practically-achievable than the value for IN718.

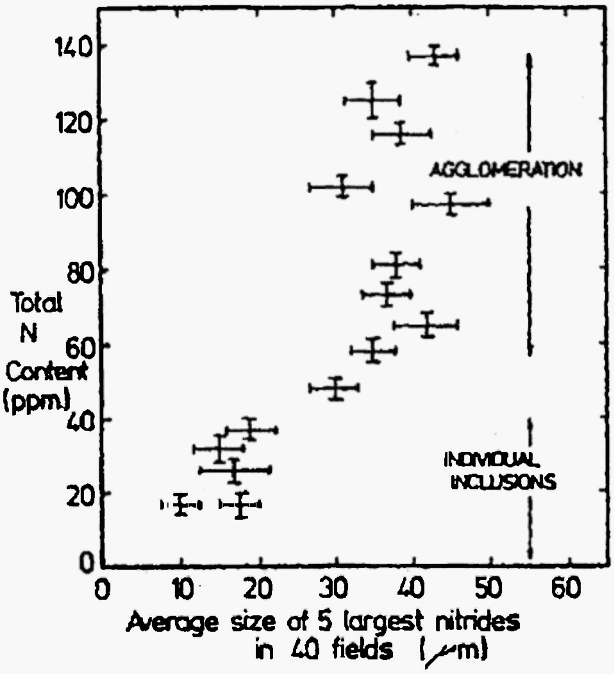


Fig. 11: Nitride agglomeration process in IN718 showing that no agglomeration occurs when the N content is below the solubility limit at the liquidus.

A second mechanism for the agglomeration prevention would be the use of a filter with sufficient surface area to collect all of the nitride. A computation of this condition however, shows that it is impractical to use a filter of low permeability (ppi > 40) since the corresponding metal flowrate would be incompatible with the casting conditions.

We can conclude, therefore, that the best route for the reduction of this problem is to provide both low-nitrogen raw materials and to use a de-nitrogenating process in the VIM.

The presence of TiN particles at the solidifying interface has been shown /10/ to provide a nucleating site for gamma-phase growth and hence to influence the conditions for the columnar/equiaxial transition and also the supercooling conditions for the nucleation of random grains in the SX alloys. In these alloys, when cast in complex shapes that have the potential for substantial undercooling it is necessary to remove all TiN particles before solidification through the use of low-nitrogen alloys. In this case the master alloy melt must be processed at pressures which ensure the decomposition of TiN and which can also remove some of the nitrogen in solution so as to prevent TiN precipitation during cooling and solidification.

5. NITROGEN REMOVAL IN THE VIM

Studies of the nitrogen exchange reaction on liquid iron or nickel surfaces are extensive /11 – 13/ and show the conclusion that on both metals, the rate of the exchange reaction is strongly influenced by the state of oxidation of the alloy. Oxygen is surface active in these liquids and effectively blocks the surface reaction:

$$2\,[\mathrm{N}]_{\mathrm{surface}} = \mathrm{N_2(g)}$$

Although the final superalloy composition has a low oxygen potential, it also has a high Ti content which will greatly reduce the activity of [N]. We must therefore remove the nitrogen before the deoxidizing influence of Ti can be applied, since the amount of TiN which will be removed from the liquid by sticking to the surface of the crucible walls is very small. The equilibrium nitrogen pressure in the reaction:

$$[\mathrm{Ti}] + [\mathrm{N}] = \mathrm{TiN\ (s)}$$

at the process temperature is of the order of 10^{-5} Bar and degassing would hence be expected to be a slow process. In the case of argon purging as bottom bubbling, the removal rate of nitrogen has been computed /14/, on both kinetic and mass-balance grounds. In this work, argon volume ratios as high as 100Nm^3/tonne are shown to be required in order to remove 20% of the nitrogen at the level of 50ppm. In the strong mass-flow regime of the induction furnace, the direct surface degassing reaction is as fast as the argon purging reaction (as shown by modelling studies /14/) and the added complexity of argon bubbling under vacuum is not justified. In a conventional 10T VIM furnace the nitrogen degassing rate of the full superalloy composition is very slow /15/, of the order of 5ppm/hr and for practical purposes any nitrogen removal must be accomplished before addition of Ti. For starting charges of 100% raw material, this procedure is practical, as the principal nitrogen source is chromium. In an example IN718 charge using 100% raw material with Cr of 90ppm N, processing through VIM (10^{-5} Bar) and VAR (1.2×10^{-5}Bar) resulted in an ingot with an average N content of 35ppm; a value close to the solubility limit of TiN at the liquidus.

However, in charges containing a high proportion of superalloy scrap the removal process is not only slow, but requires ambient pressures in the furnace which are lower than the equilibrium partial pressure of the nitrogen in solution. In a low Ti superalloy such as IN718 this pressure would be approximately 10^{-5} Bar. The difficulty of arranging this pressure regime in a large furnace is considerable and accounts in a large measure for the requirement of a low leak rate in the equipment. Since the reaction for nitrogen removal is dependent on the exposed surface area, methods have been proposed to increase the effective area by creating standing waves on the metal surface through induction coil design. The effectiveness of this technique is not reported. In addition, since the reaction is sensitive to the oxygen potential of the surface, and hence also to the oxygen potential of the atmosphere immediately above the surface, the reaction rate can be significantly increased by making additions of strong deoxidizing elements which do not form stable nitrides, such as magnesium.

6. NITROGEN REMOVAL IN ESR

ESR slags which do not contain oxides have a significant solubility for Ca_3N_2 /16/ and this effect has been proposed as a mechanism for removing nitrogen during the ESR processing of titanium alloys. The mechanism contains the reaction:

$$3(Ca) + 2TiN(s) = (Ca_3N_2) + Ti \qquad (1)$$

utilizing the solubility of both Ca and calcium nitride in liquid CaF_2 at the process temperature. In principle, the same process could be applied to superalloys, at the expense of substantial calcium solution in the alloy, but has not been reported as either experimental or pilot work. ESR slags of a more conventional composition, containing substantial amounts of oxide, have only a very small solubility for nitrogen, presumably as nitride ion, and do not dissolve TiN. In industrial processing of superalloys, however, a significant amount of nitrogen is found to be removed from the alloy and it has been found that this removal process is one of physical separation of TiN particles. The particles are driven to the melting surface of the electrode by surface tension forces and when the liquid alloy subsequent joins the ingot pool surface the particles are caught by the surface movement and swept to the meniscus at the pool periphery. At this point they are trapped on the solidifying surface and are contained in the outermost 3 – 5 mm of the ESR ingot. In this manner, an electrode of IN718 with 80ppm N is found to produce an ingot of 60ppm N, but in which the surface layer contains 300ppm N and has a visible ‘gold’ colour due to the TiN content.

Clearly, only the nitrogen content which is present as TiN particles at the process temperature can be removed in this manner and no nitrogen removal is expected or found when processing alloys with nitrogen contents at or near the solubility limit of TiN at the liquidus.

7. NITROGEN REMOVAL IN VAR AND IN ELECTRON BEAM REMELTING

The VAR process is normally carried out at operating pressures of the order of 10^{-5}Bar, and thus provides an ambient atmosphere to the melting alloy in which the nitrogen partial pressure is close to the decomposition pressure of TiN. We can anticipate, therefore, that the alloy will experience a nitrogen loss during processing which will decompose TiN, but will not further lower the nitrogen content in solution. In addition, the same physical removal mechanism as for ESR can operate in VAR, leading to a further removal of solid TiN. As a result, superalloys processed by VAR will lose some nitrogen if the content is in excess of the TiN solubility limit at the liquidus, but nitrogen removal to levels well below that limit is not to be anticipated, and is not observed in practice.

The electron beam furnace presents the same reaction scheme, but with the added complexity of lower pressures and longer residence times. The removal of nitrogen in this case is also pressure dependent, but in a regime where the ambient pressure is well below the decomposition pressure of TiN. The EB furnace also provides the added advantage of good temperature control, larger surface/volume ratio and, if necessary, long residence times in the reaction zone. It has been employed in the recycling of nitrogen-contaminated scrap in the case of the more expensive DS and SX alloys /17/, but is at present too costly to consider as a process route for the less valuable forging grades. The scrap recycling route has been shown to give very low nitrogen contents /18/ and is probably the best technical solution to the nitrogen problem.

8. CONCLUSIONS

1. The thermochemical principles of nitrogen solution/precipitation in the superalloys are well-understood, but the precise database for the required computations is not presently available. We cannot, therefore, make accurate predictions of the reaction rates and process conditions for any given alloy composition.
2. TiN precipitation plays an important role in the inclusion/carbide scheme of superalloy dynamic properties.
3. A 'superclean' superalloy could be defined as one in which the nitrogen content is below the solubility limit of TiN at the carbide precipitation finish temperature. Such an alloy would have no carbide or nitride clustering and should have properties controlled exclusively by grain structure.
4. In practical vacuum melting of the superalloys, the most effective method of nitrogen control is by the use of low nitrogen raw materials. In the case of scrap recycle melts, either we must use VIM at a low pressure (10^{-6}Bar) with enhanced processing additions, or EBCHM.

REFERENCES

1. X Huang, Y Zhang, Z Hu and Y Liu, "Thermodynamics of Inclusion Formation in Ni-based Superalloys", private communication.
2. S L Cockcroft, T Degawa, A Mitchell, D W Tripp and A Schmalz, *Electron Beam Refining,* R Bakish (Ed.), Bakish Corp, Englewood NJ USA, 1992; pp 143 – 151.
3. A K Koul, V R Parameswaran, J-P Immarigeon and W Wallace, *Advances in High Temperature Structural Materials*, NRC, Ottawa, Canada, 1994; pp 95 – 120.
4. B Ozturk, R Matway and R Fruehan, *Met Trans B*, **26B,** 563-567(1995).
5. H Wada and R Pehlke, *Met Trans B*, **8B,** 443-450(1977).
6. R Soundararajan, MASc Thesis, University of British Columbia, 1998.
7. A Mitchell and T Wang, *Superalloys 718, 625 and 706*, E A Loria (Ed.), TMS – AIME New York USA, 2001; pp 81 – 90.
8. A. Mitchell, A J Schmalz, C Schvezov and S L Cockcroft; *Superalloys 718, 625 and 706*, E A Loria (Ed.), TMS – AIME New York USA, 2001; pp 65 – 78.
9. Y Haruna, A Mitchell and A J Schmalz, *Proc, Vacuum Metallurgy Conference 1994*, A Mitchell and J Fernihough (Eds.), AVS New York, USA, 1994; pp 181 – 204.
10. T Wang, PhD Thesis, University of British Columbia, 2003.
11. L Petitnicolas, A Jardy and D Ablitzer, *Proc. International Symposium on Liquid Metal Processing 1997*, A Mitchell and P Auburtin (Eds.), AVS New York, 1997; pp390 – 402.
12. A Kobayashi, F Tsukihashi and N Sano, *ISIJ*, **33,**

1131-1135 (1993).

13. T Ikeda, K Yamamoto, T Kuranaga, T Fuji and M Maeda, *Electron Beam Refining*, R Bakish (Ed.), publ Bakish Corp, Englewood NJ USA, (2000), pp198 - 204
14. K W Lange, M Ohji, K Okohira, D Papamantellos and H Schenck, *Proc. 4th ICVM*, T Saito (Ed.), Iron & Steel Soc of Japan, 1974; pp 57 - 61
15. A Simkovitch, *J Metals*, April (1966), 504 – 512.
16. M G Benz and W T Carter, *Proc. Symposium on Advanced Technologies and Processes for Metals and Alloys*, June 16 – 17, 1999; Frankfurt, DGM Frankfurt, paper 04-2-2.
17. J Borofka and C Entrekin, *Electron Beam Refining*, R Bakish (Ed.), Bakish Corp, Englewood NJ, USA, 1991; pp 227 – 239.
18. D Hartmann and U Muerrle, *Electron Beam Refining*, R Bakish (Ed.), Bakish Corp, Englewood NJ, USA, 1991; pp 211 – 226.