Primary Carbide and Nitride Precipitation in Superalloys Containing Niobium


Department of Metals and Materials Engineering
University of British Columbia
Vancouver, BC, Canada V6T 1Z4

ABSTRACT

The primary precipitation reactions for the solidification of alloys IN 718 and IN 706 have been studied. The particular points of interest are the formation of the primary carbides and nitrides, since these particles have been found to control the fatigue and fracture behaviour of the very clean alloys presently in use in turbine disk applications.

We find that the nitride precipitates are pure TiN and contain neither Nb nor carbon quantities detectable by EDAX or WDS techniques. The carbides are mixed Nb-Ti-C carbides, but contain no nitrogen detectable by the above methods, although some nitrogen solution has been reported in the literature for similar systems. The precipitation behaviour can be rationalized in terms of the formation reactions with respect to the Ti, Nb, N and C contents of the alloy samples. The primary carbides are found to nucleate on pre-existing TiN particles. We found no evidence of carbide pushing by the solidifying dendritic interface, nor of carbide flotation from the liquid/solid zone.

In order to avoid the formation of the primary carbide particles during solidification, it is necessary either to reduce the carbon content (to < 0.006 wt% C in alloy IN 718) or to delay the carbide nucleation reaction by reducing the nitrogen content (to < 8 - 10 ppm in alloy IN 718).

The feasibility of making alloy IN 718 with no primary carbides has been demonstrated for the low carbon version; for the low nitrogen/normal carbon version made conventionally but with pure raw materials, and also by refining the alloy through electron beam processing.

INTRODUCTION

The two title alloys are widely used in high temperature application, notably as disk materials in aero-engines and industrial turbines. In the past, the general level of non-metallic inclusion content in the alloys was such that LCF (low-cycle fatigue) failure origins were almost always at these particles. The advances in clean melting techniques of the past few years have meant that the LCF crack origins are now primarily at either structural features such as grain boundaries, or at clusters of primary precipitate particles, i.e., carbides and nitrides /1/ as shown in Fig. 1. In attempting to extend the useable life of components made from the alloys, the principal barrier lies in the statistics of evaluation of these crack-starters. The individual particles are seldom of a size which will provide a mechanical effect, but they can form isolated, rare, random clusters which have the required dimensions. In high quality alloys, these clusters have a frequency of occurrence which makes evaluation by standard metallographic techniques virtually impossible; also, the size range of the clusters lies at the extreme limit of ultrasonic detection techniques in the components. For these reasons, the best solution to the quality problems probably lies in manufacturing process control, in which the precipitation of the particles is controlled to the extent that the clusters
cannot form. One version of this logic would be to use powder metallurgy or RST techniques, but since the components in question are at present made satisfactorily in all other respects by a conventional ingot/billet/forging route it is logical to examine the extent to which we can improve this method before employing a more expensive technology. The corollary to this argument is that the precipitation conditions of the carbides and nitrides must be well understood. The purpose of this work is to provide that information.

The two alloys contain carbon in the formulation (Table 1) to provide a small amount of \(M_23C_6\) carbide as a secondary precipitate at low temperature /2/. This carbide is held to be an important component in stabilising grain boundaries during creep processes, although this point is not well-established. The carbon content required for this precipitation is probably small, and almost all of the carbon content in the conventional alloy composition can be accounted for by the primary MC carbide (essentially NbC) which forms during solidification, either as discrete carbide or as part of the final eutectic reactions /3/. The primary carbides are very stable and are not altered in size or shape by the homogenisation or working treatments applied to the alloys, even though the former is normally within 25°C of the final eutectic. The carbides undergo some Ostwald ripening during prolonged homogenisation in a temperature range where some grain-boundary liquidation can be observed, but the carbide size distribution found on primary solidification is usually that to be found in the final alloy product.

The nitrogen content of the alloy is not part of the intentional formulation, but comes from the impurity levels of the raw material and contamination during melting and casting. The alloys have a range of commercial specifications and corresponding nitrogen contents. For example, in IN 718 alloys destined for

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rotating-part forgings have a range from 40 - 80 ppm, depending on the detailed end-use; the casting alloys are generally of lower values, from 15 - 25 ppm when intended for critical application, 40 - 80 ppm for less stressed parts. The reasons for this difference are not well supported in the literature, but are connected with the formation of casting defects, such as microoporosity, in casting alloys with higher nitrogen values. These defects are probably not of concern in a material which will be heavily worked. The nitrogen is present in the solid alloy as particles of TiN. There is probably some solid-solution between NbC and TiN (which have similar crystal structures), but it does not appear to be extensive in these alloy compositions, although the interface between the two compounds shows some gradation in Ti and Nb for a short distance across the boundary /4/, indicating either a co-precipitation during freezing, or a subsequent interdiffusion. Włodek /4/ reports the presence of carbo-nitrides in IN 718, as opposed to pure NbC, on the basis of diffraction data, but it is not certain that the structures reported were in fact carbo-nitrides or a mixed carbide of Ti and Nb, due to the experimental difficulties involved in the determination of carbon and nitrogen in the particles. There is strong support, however, for some substitutional solid solution of nitrogen in Ti-C-N in reports /5,6/ of studies on carbide/nitride particles in alloys not containing Nb (e.g. Nimonic 80A) in which a two-phase structure of titanium carbide containing some nitrogen and a nitride containing some carbon was determined by extraction and chemical analysis. Nitrides other than TiN (e.g. NbN) have not been reported in alloys with a niobium content.

The solubility of TiN has been extensively studied in superalloys by equilibration methods. It has been shown that the saturation solubility of TiN is, as expected, a function of the Ti and N content, but is also related to the Cr content /7/. IN 718 and IN 706 have a considerable solubility for TiN as their Ti contents are quite small, and Cr contents quite large in the general spectrum of superalloy formulations. The solubility is a strong function of temperature (Fig. 2). In a forging alloy of IN 718 with 60 ppm nitrogen, approximately 2/3 of the nitrogen content is in solution, 1/3 as precipitated solid TiN, at the liquidus temperature of the alloy; at 100°C superheat, all of the nitrogen is in solution. The implications of this behaviour for melt-processing, particularly filtering and clean powder manufacture, have been discussed /9/. A further point of note is that the agglomeration process for TiN particles, necessary to form the inclusions which influence mechanical properties, can only take place when the particles are free to move through the liquid alloy. The extent to which this process can take place within a solid/liquid mushy zone is not known, but in the limit if no precipitated TiN is present before the alloy is fully solidified, then no agglomeration can take place. This proposition has been used /7/ to suggest that a nitrogen content of less than 5 ppm would be a level in IN 718 at which no TiN agglomerations could be found, and should, therefore, be an aim level for defect-free material in which the freedom from crack-starting inclusions was assured by chemical analysis alone. This value was obtained by extrapolation of the thermochemical information on the liquid alloy, taking into account segregation during freezing, but not accounting for any possible solution of nitrogen in the carbide. Should the NbC precipitated during freezing contain a significant amount of nitrogen, the permissible value quoted above would be increased.

The carbide solubility is also a strong function of

![Fig. 2: Temperature dependence of the saturation solubility of TiN in IN 718, from ref. /8/.
I – solubility in the bulk alloy composition;
II – solubility in the interdendritic liquid, taking into account the segregation of Ti and N.](image-url)
temperature, and has the expected relationship to niobium and carbon content, as will be seen below. Generally, however, niobium carbide is completely in solution at the liquidus temperature in these alloys and its precipitation behaviour is connected entirely with composition and temperature changes occurring during the freezing process. There are no reports of solid carbide particles existing in the liquid phase in these alloys, or of carbide particles remaining undissolved during the melting/casting sequence.

The phase structure of IN 718 during solidification has been studied by the DTA method /10/ and it has been concluded that in the conventional formulation with respect to Nb and C, the carbide precipitation-start temperature is reached when the alloy is approximately 70% solid, and continues until the final series of divorced eutectics, which produce, first, gamma plus NbC, followed subsequently by gamma plus NbC plus Laves phase. A typical microstructure resulting from this sequence is shown in Fig. 3, in which the secondary precipitation of needles of delta phase can also be seen, originating from the eutectic region. During all of this process, there is strong segregation of niobium, titanium and carbon into the interdendritic liquid. The carbide particles which are of concern in mechanical properties are those which precipitate between the carbide-start temperature and the first eutectic, since these have the largest size.

It has been shown /11/ that the primary carbides in the conventional alloy invariably contain a core of TiN, as illustrated in Fig. 4, although not all nitrides are surrounded by precipitated carbide. There is clearly a relation between the two precipitation reactions, probably due to the close match in isomorphicity between the compounds, although in the conventional compositions of the alloy the nitride invariably appears to precipitate before carbide. There is no reported instance of a carbide surrounded by precipitated nitride, possibly because in the alloy composition required to effect this precipitation sequence, the nitrogen would all be taken into solution in the Ti-Nb-C carbide structure.

The following study reports in detail on the precipitation conditions for the primary carbide and nitride over a range of alloy compositions for the general alloy formulation of IN 718, and also on some results for the similar alloy IN 706.

**EXPERIMENTAL**

Composition variations (Table 2) on the two alloy systems were investigated, with the principal variations being in C, Nb, and N. The alloys were prepared by vacuum induction melting in alumina or magnesia crucibles.

![Fig. 3: Microstructure of as-cast IN 718, showing: a) Laves phase; b) primary carbide; c) delta phase.](image)
Fig. 4: a) Structure of "TiN" precipitate, showing the oxide core and carbide growth.

Fig. 4: b) and c) Titanium EMPA analysis indicating TiN core and NbC envelope.
Table 2
Alloy compositions

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The experimental methods used were:

**Directional solidification/quench (Fig. 5)**

The DS technique used was the classical Bridgeman method, with vertical withdrawal. The sample was placed in an alumina tube of 5 mm i.d. and gradually lowered through the induction heated susceptor in a vacuum enclosure. The required DS conditions were established by calibrating the furnace using a Pt/Pt-RH thermocouple placed inside a similar metal sample during the DS process. The variables used were the temperature gradient and the withdrawal rate. The sample was fully liquid with 100°C superheat for approximately 20 minutes before the DS system was started. When the DS zone had been established the sample was rapidly lowered from the furnace into a quench zone consisting of either a water-cooled copper block, or a bath of Woods metal held at 200°C. The solid sample was then sectioned for examination of the DS zone.

**Unidirectional solidification (Fig. 6)**

The unidirectional solidification was accomplished by melting the sample by induction under vacuum in situ in an alumina tube which was closed at the base by a combination of steel and water-cooled copper chill. At the commencement of the experiment, the sample was liquid up to a thin chill-layer of solid on the base. The input power was then gradually decreased, at a pre-determined and calibrated rate, to establish the required solidification conditions of rate and temperature gradient.

**Electron beam button melting and cold-crucible melting (Fig. 7)**

The equipment used was the UBC 40 kW EB furnace, previously described in the literature /8/. The samples were fed into the melting zone as illustrated in
Fig. 6: Outline diagram of the equipment used for the CET experiments.

Fig. 7: Outline diagram of the EB button melting/refining equipment.

Fig. 7, to make a refined small static-cast ingot. This sample was then used as the starting material in the two systems described above, after careful removal of the inclusion cap. During the EB melt, care was exercised to apply the minimum power required for melting so as to minimise the effect of inclusion dissolution and re-precipitation during the process.

The cast structures were examined by conventional metallography, SEM-WDS and EDAX, DTA and by EPMA, with check chemical analyses on the final cast structure carried out as appropriate.

Alloy IN 718

The carbide precipitates may be grouped into two kinds, primary and eutectic, illustrated in Fig. 8. The primary carbides, showing a core of nitride, are easily distinguished in optical metallography by their colour; the nitride core is golden, the carbide envelope is greyish-pink. The core shows very little Nb content and corresponds in analysis to stoichiometric TiN, as do the isolated nitride particles which do not have carbide envelopes. The carbide exhibits some Ti content and Nb content variation, as shown in Fig. 9. It is evident that the eutectic carbide is essentially stoichiometric NbC, but that the primary carbide is a mixed Nb-Ti-C compound, with a Ti/Nb ratio of approximately 0.13. Within the detection limits of EPMA for nitrogen in the presence of titanium, no nitrogen could be detected in the carbide region (< 5 wt%), and the carbide is presumed to be a mixed carbide in which the Nb/Ti ratio is approximately 5, with the possibility that the carbide may contain less than 5 wt% N in solid solution. (This quantity of nitrogen would be insufficient to change the lattice parameter to a degree detectable in electron diffraction, and chemical extraction followed by X-ray diffraction would be complicated by the need to separate selectively both TiN and the eutectic carbides from the primary carbide residue - a procedure which has not yet been developed.) In the many carbides examined, this composition pattern appeared to be constant, and not influenced by alloy Nb/Ti ratio, carbon content or freezing conditions over the ranges applied. It is interesting to note that although the carbide (whether it is NbC or Nb-Ti-C) has a density considerably lower than that of the liquid alloy, we found no evidence of carbide particles floating out of the freezing interface, in contrast to the finding of TiN flotation in IN 100/11. This could have been due to the vertical temperature gradient, which would promote resolution of a rising particle, or alternatively to the fact that the dendrite network is relatively dense at the temperature of the carbide precipitation start. The carbide distribution (Fig. 10) obtained from DSQ samples...
shows the increase in carbide fraction as the solidification proceeds, and the relation of the precipitation reaction to the solid fraction and niobium concentration in the remaining liquid /7/. In the final solid structure, approximately 80% of the carbide particles were found within primary dendrite envelopes, the remaining fraction being part of the final eutectic reactions. This finding indicates the absence of any carbide particle pushing during the dendrite growth.

The average carbide size was measured metallographically, using the method of Ballantyne et al. /12/, with the results shown in Fig. 11. It will be seen that the size range may be correlated approximately to the time interval between the carbide precipitation start and the time at which the system finally solidifies, through the dendrite spacing. The largest dendrite spacing examined has a local solidification time which is equivalent to that found in the mid-radius position of a typical 500 mm diameter industrial VAR ingot of this alloy. We expect that the observed carbide size range in the experimental alloys between primary dendrite spacings of 200 and 400 microns would be that observed in the equivalent portions of commercial VAR ingots. The effect of lowering the carbon content can be clearly observed and represents a very significant microstructural change in respect of the largest carbides, and also in respect of the quantity of carbide present. It is to be noted that the size of the largest primary carbides does not change substantially until the carbon content is reduced to below 0.01 wt%, at which point the size diminishes markedly.

Repeated polishing to remove a few microns of alloy was used to establish that the primary carbides invariably contained a nitride core when both the nitrogen and the carbon contents were relatively high (0.008 wt% < C < 0.06 wt%, 15 ppm < N < 100 ppm); the core was not observed in the eutectic carbides. In the alloy samples of very low carbon and nitrogen content, this effect could not be established; at the lowest nitrogen levels the nitrides were completely absent and at the lowest carbon levels there were no primary carbides. The nucleating effect of TiN on the primary carbide has been noted previously, but it is interesting to observe the changes which take place in the alloy when the nitrides are absent. Total suppression of the nitride precipitation requires reduction of the nitrogen
Fig. 9: Nitride/carbide particle and analysis.

Fig. 10: Distribution of carbides during solidification.
content into the range of 5-8 ppm N /7/, at which level TiN will not precipitate above the eutectic temperature in spite of the strong segregation of titanium in the interdendritic liquid /7/. Two alloys were prepared with conventional Nb content (5.3 wt%) and carbon content (0.03 wt%) alloy X, treated by electron-beam melting to lower the nitrogen content, and alloy Y manufactured from extremely pure raw materials so that both had nitrogen contents which were in the critical range (5 - 8 ppm) and did not exhibit TiN precipitation. In these two alloys, the eutectic structure was altered from the normally-observed Laves (A$_2$B) + NbC + gamma, to a different structure in which the Laves was largely replaced by delta phase (essentially Ni$_3$Nb), as shown in Fig. 12. In these cases, suppression of the primary carbide precipitation by removing the nucleation sites

![Fig. 11: Variation of carbide size in relation to the freezing rate.](image1)

![Fig. 12: Eutectic structure of the as-cast alloys (a) #82 and (b) X and Y. X had the normal IN 718 composition, with 0.03 wt% C, but was treated by EB melting to remove nitrogen down to 4 ppm. Alloy "Y" had the same composition, but was manufactured from very high purity raw materials to give a nitrogen content of 4 ppm.](image2)
has changed the niobium and carbon content of the final liquid to solidify to the point at which the delta phase becomes the more stable composition. This interpretation agrees with the sequence of solidification proposed by Radakrishnan /3/, based on the Ni-Nb-C phase diagram.

When TiN is present, the precipitation of the primary Nb-Ti-C phase may be represented by a "solubility product", (wt% Nb) x (wt% C), since the Ti content is approximately constant. The boundaries for this reaction are shown in Fig. 13, and were obtained by metallographic examination of the solid DS samples. The onset of carbide precipitation is difficult to detect by the DTA technique in very low carbon alloys since the volume fraction of carbide is not large enough to produce the required thermal effect and also since the precipitation takes place over a range of temperature below the carbide start temperature /10/. The relationship determined from Fig. 13 for the precipitation boundary of NbC in alloy IN 718 is:

\[ [\text{wt} \% \text{ C}] \times [\text{wt} \% \text{ Nb}] = 0.21 \]

(Compositions given are the alloy bulk composition)

which defines the boundary between compositions which will, or will not, precipitate primary NbC. The product given above should not be compared with any value derived from the thermochemistry of the segregated solidifying alloy composition, since the actual C, Ti and Nb concentrations prevailing at the temperature of precipitation are very different from the bulk concentration due to segregation. Previous work /7/ has demonstrated that the conventional alloy composition solidified under conditions giving a primary dendrite spacing of approximately 300 microns produces a liquid of approximately 10 wt% Nb, 3 wt% Ti and 0.2 wt% C at the temperature of the start of the carbide-forming reaction. This latter composition can be rationalised with the known thermochemical data for carbide stability if there is a substantial negative deviation from ideality in this solution and in the precipitated mixed carbide, since the reaction:

\[ \text{TiC(s)} + \text{[Nb]} = \text{NbC (s)} + \text{[Ti]} \] (2)

has an equilibrium constant; K (1800K) = 0.13.

The DTA data for the alloys support the above conclusions, and are shown in Fig. 14. It is seen that as the carbon content is decreased the first eutectic temperature increases until, at the lowest carbon contents, it is above the nominal carbide precipitation temperature. Applying a simple Scheil analysis to the segregation of carbon in the alloys indicates (as shown in Fig. 15) that in the lowest carbon compositions, segregation will not produce a liquid of the critical 0.2 wt% carbon before the eutectic temperature is reached. The carbide precipitation, therefore, does not take place in these alloys.

ALLOY 706

This alloy is distinguished from IN 718 by two principal features: the much higher iron content, and
the higher Ti/Nb ratio. The quantity of primary MC carbide generally observed is significantly less than that found in IN 718, but the metallographic appearance is quite similar and the mechanical effects are probably also the same in the two alloys.

The primary carbide is found to nucleate on TiN, and the composition of both carbide and nitride phases was determined. As was the case with IN 718, the nitride phase contains very little Nb and is essentially stoichiometric TiN. The carbide phase is a mixed carbide Nb-Ti-C, in which, within experimental error, the Ti/Nb ratio in the primary carbide is the same as that found in IN 718 in spite of the very different Ti/Nb ratio in the alloy. The alloy contains a smaller volume fraction of primary carbide and nitride than does IN 718, probably because of the increased iron content, which would be expected to increase the solubility of both N and C in the gamma matrix.
DISCUSSION

From the analysis presented above, it is possible to make several observations pertinent to the use of the two alloys, and also to other similar alloys such as IN 625 and to potential alloy development.

First, to address the basic problem of removing the primary carbide/nitride clusters which are the pre-eminent cause of LCF failure in the present alloy, we must evidently delay carbide precipitation until the first eutectic temperature, or reduce the carbon level to the point at which the precipitation reaction does not take place, or solidify the alloy at a rate which prevents carbide precipitation in the particle size range of interest. The best alloy formulation, at least for conventionally-solidified material, is probably a combination of the first two methods. In alloy IN 718, the nitrogen content should be reduced to a level of below 10 ppm, at which point nucleation of the precipitation reaction is brought to a practical minimum. At the same time, the carbon level in this alloy should be reduced to below 0.008 wt%, at which point the amount of primary carbide precipitated is very small. The questions of the effect of these changes on the amount of secondary M23C6 precipitates present in the final alloy component; the control of delta-phase solution and re-precipitation and both of their consequent effects on mechanical properties, have yet to be answered. The same principles also apply to alloy IN 706, but in this work we have not experimentally defined the appropriate limits for C and N. It is likely, in view of the alloy composition, that the levels for effects equivalent to those in IN 718 will be at somewhat higher C but lower N contents. For alloys which have been atomised or rapidly-solidified, these considerations are not appropriate as the freezing rate itself appears to suppress primary carbide precipitation /14/; the carbides so formed are not found to grow during subsequent consolidation or heat-treatment.

The second point of note is that the mixed carbide composition found in these alloys appears to have a Ti/Nb ratio which is independent of bulk alloy composition. This effect is probably a reflection of the liquid composition at the temperature of carbide formation, since both Nb and Ti segregation in IN 706 are less severe than that found in IN 718.

The third point concerns the role of that content of nitrogen which is not present as observable titanium nitride precipitates. We have not found any positive evidence of nitrogen solubility in the mixed primary or eutectic carbide, but at the expected levels (corresponding to the solubility of TiN in the liquid at the first eutectic, i.e., 5 ppm N), the content of nitrogen dissolved in the carbides being precipitated at this temperature would not be detectable by any of the methods used here or in previous work. It seems quite probable, however, that the carbides which precipitated late in the solidification sequence contain the residual nitrogen, as opposed to a fine dispersion of TiN present in the eutectic structure, and are therefore carbonitrides. For the same reasons, the carbonitrides identified by Wlodek /4/ by extraction from freckled areas in IN 718 could possibly have been formed from a liquid which was richer than normal in nitrogen due to segregation, and lower in carbon than normal due to the physical separation of primary carbides from the freckle-forming liquid in the flow process.

The final point of note is that the primary carbide contains only 20% of the total carbon content of the alloy, and a very small part of the Nb and Ti content. Changes in the bulk alloy composition with respect to these elements are unlikely to influence the basic reactions of formation of delta and gamma phases, except through their influence on the eutectic reactions and the homogenisation of the Laves component /15/.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge support of this research by the Nickel Development Institute, the Natural Sciences and Engineering Research Council of Canada, Special Metals Corporation and SNECMA. The assistance of Inco Alloys International in providing some of the experimental alloys also contributed to the success of the programme.

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