" FRECKLES " IN CAST AND WROUGHT PRODUCTS

S.T.Wlodek* and R.D. Field** GE Aircraft Engines, Cincinnati 45215, OH.

Abstract

"Freckles", the microstructural condition that results from the inverse segregation of niobium in gamma double prime strengthened nickel - iron base alloys, are described for a large alloy 718 casting and an alloy 706 forging. In both cases, large carbonitrides and Laves phases, that formed in the liquid state, were the deleterious phases present.

The 718 freckle extended over a volume of some $20~\rm cm^3$, and exhibited a 150% increase in Nb and Ti. It consisted of semi-continuous chains of Laves outlining the grain boundaries, with intragranular delta plates throughout the whole structure. Delta precipitates were also common inside the Laves particles, which typically averaged $40~\mu m$ diameter. Nb rich MC and high Cr M₃B₂ phases were also found.

The freckling in the alloy 706 forging consisted of linear indications some 0.5 mm wide and present at a density of 4 per cm. In the freckled area, the Nb and Ti level had been increased by about 65 % resulting in the presence of heavy concentrations of Nb, Ti (C, N) and Laves, up to 17 area % in the fatigue fractures, and a matrix penetrated by delta plates. Large carbonitrides were the most deleterious phase, resulting in the nucleation of secondary fatigue cracks and a two fold increase in hold time fatigue crack growth rate.

* Gamma Prime Consultants, San Diego, CA 92127-1272. **Los Alamos National Laboratories, Los Alamos, NM 87545.

Introduction

Although the mechanism of freckle formation has been well understood since the studies of Flemings and his associates ^(1,2,3) and further amplified by Copley et al ⁽⁴⁾, their structural characteristics have essentially escaped detailed consideration, the two exceptions being a description of freckles in DS and monocrystal Udimet 700[®] and Mar- M200[®] ⁽⁴⁾, and alloy 718 VAR and ESR ingots ⁽⁵⁾. We therefore wish to describe two cases of freckling: one in a large alloy 718 investment casting, one in an alloy 706 forging. Both alloys were originally developed by International Nickel Co. as Inconel[®] alloy 706 and Inconel[®] alloy 718.

The term freckle is used to describe an area of inverse segregation that results from the movement of rejected, solute rich, liquid in the mushy zone and it's entrapment. Freckling can thus occur in any cast structure ranging from a monocrystal blade to a multi - ton ingot. The formation of freckles is promoted by low growth rates and low thermal gradients. Mathematical models that can predict the relationship between the growth rate, the thermal gradient, and the incidence of freckling have been established $^{(1-4)}$. As freckling in alloys is aggravated in systems that have a large density difference between the liquid and solid phases in the mushy zone, as well as low solute diffusivity and low viscosity, the tendency to freckling is particularly high in Ni-Fe-Nb type alloys strengthened with DO_{22} , γ'' and Ll_2 , γ' .

Although the practical measures that are required to control freckling are well understood ⁽⁶⁾ these defects still do occur. Freckling does not always involve associated porosity or non metallic inclusions and thus is particularly difficult to detect by conventional non - destructive techniques. Macro - etching is generally the most reliable procedure of assuring the absence of this defect, whose X- ray absorption coefficient can vary only slightly from that of the sound alloy. In addition, freckle formation usually involves the formation of large, brittle phases which often are concentrated heavily enough to reduce toughness sensitive properties such as fatigue. The industry trend is to ever larger turbines, and thus larger components. The challenge to achieve the high solidification rates and high thermal gradients required to produce larger, freckle free, castings and ingots will thus become harder to meet.

Experimental

Both the alloy 718 casting, and the alloy 706 alloy forging, were well within their pertinent chemistry specifications. The presence of freckling was observed during macro - etching operations and, in both cases, the material involved was scrapped. A range of standard examination techniques were utilized including: macro - examination, ultrasonic imaging, optical microscopy, scanning electron microscopy (SEM) in both the secondary electron (SE) and back scattered electron (BSE) image mode, wavelength and energy dispersive x-ray analysis, x-ray diffraction on extracted residues, and analytical electron microscopy (AEM), including selected area electron diffraction (SAD), convergent beam election diffraction (CBED) and dark field (DF) examination.

Alloy 718 Investment Casting.

The freckle that was found in a large, structural, investment casting is illustrated in Figure 1. It was located close to a gate and extended over a volume of $20~\rm cm^3$. The average chemistry of the freckled area, as determined by semi - quantitative energy dispersive x-ray analysis, was: 49.5 % Ni, 14.4 % Fe, 17.1 % Cr, 13.3 % Nb, 3.3 % Mo, 1.7 % Ti, and 0.7 % Al, in weight per cent.

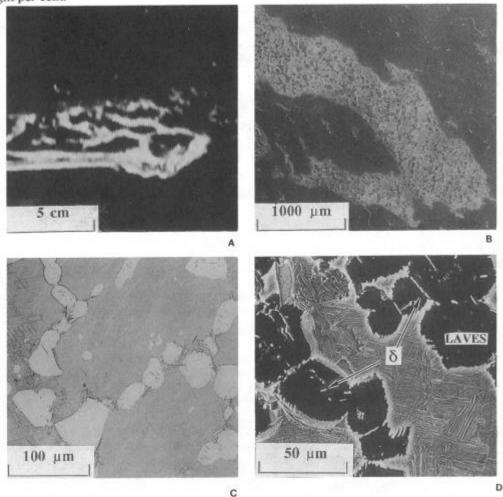


Figure 1. Characterization of freckle in cast alloy 718. See Figures 2 to 4 for AEM data .

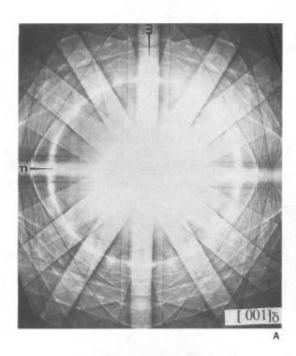
A. Sonic image . B. SEM /SE image. C. SEM / BSE and D. SEM / inverse BSE image.

Note continous bands of Laves, along grain boundaries ,with small delta plates precipitated in the larger Laves particles, and a matrix completely penetrated by transgranular delta plates.

The phases portrayed in Figure 1 were identified using AEM procedures. Figure 2 presents the data identifying the delta plates, where DF examination confirmed that all the plates possessed the orthorhombic DOa structure ($a=0.52~\rm nm$, $b=0.43~\rm nm$, $c=0.45~\rm nm$), that was established by SAD and CBED techniques. Figure 3 summarizes AEM techniques which identified the globular phases that exist in grain boundary arrays as Laves (C14 structure, $a=0.48~\rm nm$, $b=0.80~\rm nm$), while the small plates that had precipitated in some of the larger Laves phases (see Figure 1 C) were identified as delta by diffraction and DF imaging . The average chemistry of the Laves phases, obtained by energy dispersive x-ray analysis, was : 38.9 % Ni, 13.1 % Fe, 15.0 % Cr, 25.5 % Nb, 6.8 % Mo, and 0.8 % Ti, all in wt per cent.

The minor phases in the freckle were also identified by AEM procedures as an MC (B1, a = $0.45\,$ nm) and a M3 B2 (tetragonal a = $0.59\,$ nm, c = $0.33\,$ nm) whose SAD and CBED patterns are given in Figure 4. The boride was usually found to be nucleated on a MC phase. The metallic analysis obtained on the MC carbides was 88.6 wt % Nb, 7.3 wt % Ti and 0.6 wt %

Mo.





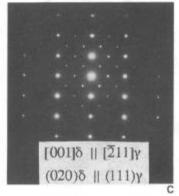
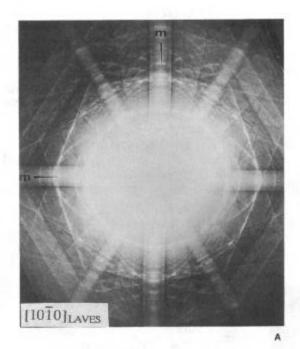


Figure 2. AEM identification of delta.

A. CBED of [001] zone axis from delta plate showing 2mm symmetry.

B.SAD of δ plates in γ matrix.

C. DF of δ plates indicates all are DO_a.



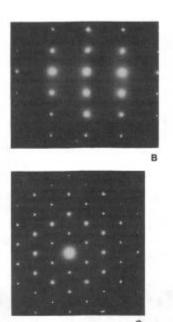
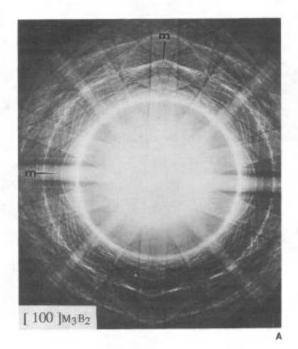


Figure 3. AEM study of Laves phase. A. CBED of [1010] zone axis showing 2mm symmetry. B. SAD [1010] zone axis.
C. SAD [0001] zone axis.
DF examination and diffraction proved that the small tabular precipitates inside the Laves phases shown in Figure 1D were δ.



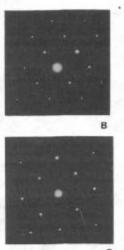


Figure 4. AEM identification of M₃ B₂
A. CBED of [100] zone axis from M₃ B₂
particle showing 2mm symmetry. B. SAD of [110] zone. C. SAD of [100] zone. These small borides were usually found

nucleated on MC phases.

Alloy 706 Forging

A large 706 alloy spacer forging, produced from an ingot that had been consolidated through VIM + ESR, was found to exhibit a heavy concentration of freckles, that were revealed by macro - etching to be linear in form, with the stringers lined up in the working direction. The linear density of stringers was as high as 4 per cm. Parallel fatigue evaluations found that the material exhibited a two fold increase in hold time crack - growth rate, over a defect free specimen, when tested with the EDM notch at the location of a known freckle, and parallel to the freckled plane. The freckled structure is illustrated in Figure 5. The arrows in Figure 5 B indicate the area where a microbeam, wavelength dispersive analysis was taken. The beam was collimated to $10~\mu m$ diameter and analyses were taken every $10~\mu m$. The scan, shown in Figure 6, was verified by additional traces, and indicated that in the freckled area the average analysis in weight per cent was : 40.6~% Ni, 35.9~% Fe, 15.6~% Cr, 2.9~% Ti, 4.8~% Nb, and 0.2~% Al.

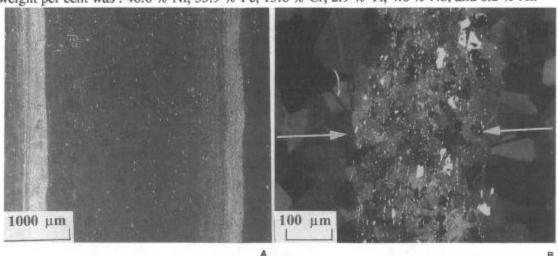


Figure 5. Appearance of linear freckles in alloy 706 forging. The density of these linear defects was about 4 per cm. Sample electro - polished and etched in metholic - 10% HCl. A. SE, SEM image. B. BSE image, arrows indicate area of micro - probe scan.

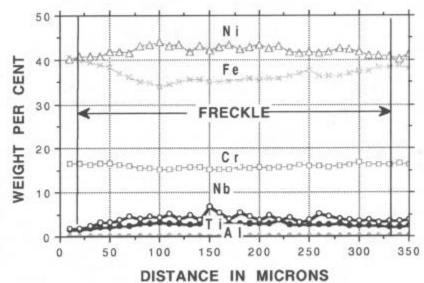


Figure 6. X-ray wavelength dispersive analysis taken across the freckle so as to avoid large MC phases. See Figure 5.

A section containing a number of freckle lines was masked so that only the phases in the freckled areas could be extracted electrolitically. The resultant extraction was separated into a coarse and fine fraction and examined in a Debye - Scherrer x - ray camera. The coarse fraction turned out to be a B1 structure, a = 0.423 nm. In the fine fraction the predominant phase was Laves, C14 (a = 0.4797 nm, c = 0.7810nm), and a few weak lines that could be indexed as delta (DOa). The extracted residues were then subjected to SEM examination and energy dispersive x-ray analysis. Figure 7 presents the appearance of the extracted residues. The {1111 pyramidal faces of the carbides was clear proof that this structure formed in the liquid. Even after undergoing electrolytic extraction, washing and centrifuging, the Laves phases were still often found joined into grain boundary chains, a condition that is also suggestive of growth from a liquid.

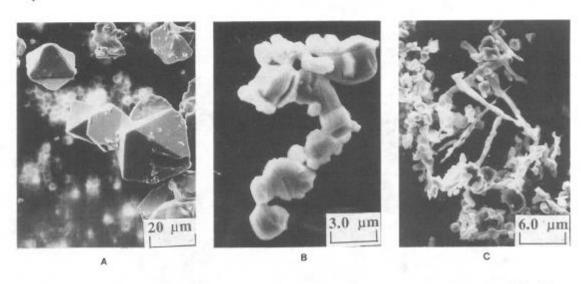


Figure 7. Appearance (SEM) of phases extracted from alloy 706 freckle for x-ray diffraction identification.

A. Carbonitride, note well developed octahedral faces indicating these phases grew from the liquid phase.

B. The Laves phases frequently formed chains of continuous particles.

C. Acicular phases, lying on a matrix of Laves chains, are probably delta.

The coarse and fine extraction residues shown in Figure 7 were subjected to standardless, semi quantitative, energy dispersive x-ray analysis. The metallic content of the carbonitride particles averaged 70 % Nb, 18 % Ti and the analysis also showed these phases to be N rather then C rich. The previous microprobe analyses, which are much more accurate, indicated that the total metallic content was: 69.1 % Nb, 17.5 % Ti, 0.3 % Fe, 0.4 % Ni and 0.2 % Cr, all in weight per cent, suggesting that the total N+C level was about 12.5 wt %, approximately 50 at %. The Laves phases analyzed as: 26.9 % Ni, 30.8 % Fe, 10.6 % Cr, 29.0 % Nb, and 2.4% Ti, all in weight per cent. This indicates that the proper formulation for this phase was : (Fe, Ni)2(Nb, Cr, Ti). The acicular phase shown in Figure 7 C was too intimately associated with the Laves

phases to allow a clean analysis.

After electropolishing and etching in metholic-10 % HCl, a SEM examination was performed of the hold time fatigue fracture surfaces. This allowed the examination of the alloy structure just below the fatigue fracture plane. In this way it was possible to associate the initiation of secondary cracking predominantly with the large carbonitrides, some of which were up to 60 µm in diameter. The Laves phases, which in this structure were 1 to 5 µm diameter, acted only rarely as crack nuclei. When secondary cracks were observed originating at Laves phases this may have been due more to their continuous, chain like, structure then their physical size. Image analysis indicated that the fatigue cracks in the test specimens had grown through freckled material where 17 % of the crack area consisted of carbonitrides and Laves. These observations are portrayed in Figure 8 which shows a typical cracked carbonitride and Laves phase colony revealed just below the fracture surface by the above electropolishing procedure.

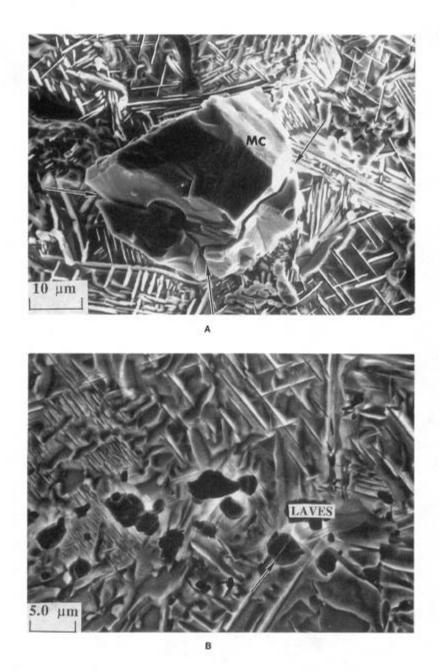


Figure 8. Microstructure of freckled area in alloy 706 just below the fatigue fracture plane, as revealed through SEM examination of the fracture, after electrolytic polishing and etching in metholic - HCl.

A. Typical cracked Nb rich carbonitride. SE image.

B. Colony of Laves precipitates. Arrow indicates small crack. Inverse BSE image. The higher atomic number Laves phases appear black.

__

Table 1 Summary of Structural Data

<u>Alloy</u>	Area/Phase	Structure	Lattice Parameter			Analysis, Atomic Per Cent				
			nm	Ni	Fe	Cr	Nb	Ti	Al	
718	Nominal Average			52.4	19.2	21.2	3.2	1.1	1.1	
718	Freckle Average			50.5	15.5	19.7	8.6	2.1	1.6	
718	Laves	C14	a = 0.48, b = 0.80	42.7	15.2	18.7	17.8	1.0		
718	MC	B 1	a = 0.45				86.0	13.2		
718	delta	DO_a	a = 0.52, $b = 0.43$, $c = 0.45$							
718	$M_3 B_2$	Tetrg.	a = 0.59, c = 0.33							
706	Nominal Average			38.9	39.4	17.4	1.8	2.1	0.4	
706	Freckle Average*			39.4	36.6	17.1	2.9	3.5	0.4	
706	Laves	C14	a = 0.4792, c = 0.7810	24.3	34.9	12.9	19.9	3.2		
706	$M(C, N)^*$	B1	a = 0.4423				80.0	20.0		

^{*} These analyses are based on quantitative, wavelength dispersive, x-ray analyses. The nominal average analyses reference freekle free alloy and are calculated from the nominal weight per cent published data and presented simply for compar purposes. All other analysis results are based on the average of at least six standardless, semi - quantitative, energy diray analyses performed either on extracted phases or phases large enough to limit the matrix contribution.

Discussion

The phases identified in the freckled areas of an alloy 718 structural investment casting, and a large alloy 706 forging, are summarized in Table I, in terms of their structure and chemistry. To allow easier comparison, the average analysis of each freckled area and the average nominal analysis of each alloy are also included, all in atomic per cent. In this study it was not possible to obtain a definitive identification of the acicular or plate like constituent in the alloy 706 freckle. It is likely that this phase is delta, possibly with some eta.

Even though the cast alloy 718 freckle involved a 150 % increase in Nb and Ti, while the wrought alloy 706 freckle involved a 65 % increase in these elements, the phases found in each freckle were the same as are common to these alloys in the normal condition. This can be said with greater certainty for alloy 718, for which a considerable amount of structural data exist, (7) then for alloy 706. In both alloys the formation of freckle structures involved the segregation of the elements that are characterized by the smallest distribution coefficient or partition ratio (C_S / C_L). The identification of an M₃B₂ precipitate in the cast alloy 718 freckle reflects either the higher boron level in the cast version of the alloy, or just a segregation effect. Borides have been found in similar cast alloys⁽⁸⁾ at a comparable boron level (0.003 to 0.004 wt %). It is interesting to note that the structure of the delta plates in the 718 alloy freckle consisted solely of the DO_a structure, exactly as in the homogeneous alloy.

Even though the chemistry of the two alloys and the amount of segregation found in their freckles were appreciably different, the two major phases that were in both freckled structures were essentially the same. The phases that comprised the freckle fracture were a Nb rich monocarbide, or carbo - nitride, and a Nb rich Laves phase. Both phases existed in a gamma matrix strongly decorated with delta plates, but fractographic examination indicated that the delta constituent was not a major initiation site for fatigue cracks. Fractography, at least of the fatigue fractures that were generated in the 706 material, indicated that the B1 type carbo - nitrides, because of their size, and to a lesser extent the Laves colonies, because of their continuous chain - like structure, are the most deleterious crack nucleating features during fatigue loading. The chain like morphology of many, but not all, of the Laves colonies strongly suggests that these phases formed from the liquid state.

Slight chemistry changes will have little effect on Laves phase formation in alloys such as 706 or 718. Although the formation of Laves phase can be promoted by high silicon ⁽⁹⁾ levels, the formation of Laves in the chemistries studied here is strictly due to the presence of Fe and Nb ⁽¹⁰⁾ and should be expected in any Ni - Fe - Nb alloy, regardless of the impurity level or the presence of other Laves formers such as Mo and Cr. Laves phase, for instance, does not form in similar Ni - Co -Nb based alloys, that do not contain any appreciable amount of Fe, such as Rene' 220 ⁽⁸⁾

The situation with the B1 carbides or carbo - nitrides is not quite the same. Any alloy containing almost any level of carbon, or other interstitials, and even very low amounts of Nb and Ti will form these constituents, usually through precipitation from the liquid. The Nb - Ti mono - carbides, mono - nitrides, and mono- oxides all form B1 type phases and they are thus very miscible with each other in the B1 structure. Contamination of a heat by N or O will thus increase the amount of MC type, carbo - oxy - nitrides as much as a proportionate increase in carbon. If freckling should occur in a heat that has a high interstitial content, the effect of freckling on properties can be exacerbated. This appears to have happened with the heat of alloy 706 studied here. One more interesting point can be made about the B1 phases. In both conventional 718 (7) and 706 the monocarbides are of two types, one high in Nb, the other high in Ti. The difference in chemistry may reflect either a difference in the temperature of formation, or a difference in supersaturation. In freckled structures only a high Nb version of this phase was observed in both alloys. The pyramidal form of these phases, with well developed { 111 } strongly suggests that they formed from the liquid state, probably in the higher temperature range of the mushy zone. Their high Nb content may thus reflect a high temperature of formation.

Acknowledgment

The work on alloy 706 was sponsored by the GE Turbine Group, Schenectady N.Y. The x-ray determinations quoted here were performed by Dr. M. Kelly, while Mr. M. Cannon was responsible for the microprobe analyses. The authors are indebted to the management of the Engineering Materials and Technology Laboratories, GE Aircraft Engines, for permission to publish this paper.

® Udimet, Mar- M, and Inconel are, respectively, registered trade marks of Special Metals Inc. Martin Marietta Corporation and International Nickel Co.

References

- 1.M.C.Flemings and G.E. Nereo, "Macrosegregation, Part I" , Trans. AIME, (1967), 239, p.1449.
- 2. M.C. Flemings, R. Mehrebian, and G.E. Nereo, "Macrosegregation, Part II", <u>Trans. A IME</u>, (1968), <u>242</u>, p.41.
- 3. M.C. Flemings and G.E. Nereo, "Macrosegregation, Part III", <u>Trans. AIME</u>, (1968), <u>242</u>, p.50.
- 4. S.M. Copley et al., "The Origin of Freckles in Unidirectionally Solidified Castings", Met. Trans., (1970), 1, p.2193.
- 4. A.F. Giamei and B. H. Kear," On the Nature of Freckles in Nickel Base Superalloys", <u>Met. Trans</u>., (1970), <u>1</u>, p.2185.
- 5.K.O. Yu, J.A. Domingue, G.E. Maurer and H.D. Flanders, "Macrosegregation in ESR and VAR Processes", J. of Metals, (1986), 38, #1, p.46.
- 6. K.O. Yu and J.A. Domingue, "Control of Solidification Structure in VAR and ESR Processed Alloy 718 Ingots", <u>Superalloy 718 Metallurgy and Applications</u>, E.A. Loria ed., TMS, (1989) p.33.
- 7. S.T. Wlodek and R.D. Field, "The Effects of Long Time Exposure on Alloy 718", Superalloys 718, 625, 706 and Derivatives, E.A. Loria ed., TMS, (1994), in publication.
- 8. S. T. Wlodek and R.D. Field, "The Structure of Rene' 220C", <u>Superalloys 1992</u>, S. D. Antolovich, et al ed., TMS, (1992), p.477.
- 9. S.T. Wlodek," Embrittlement of a Co Cr W (L 605) Alloy", <u>Trans, ASM</u>, (1963) <u>56</u>, p.287.
- 10. F. Laves and H.J. Walbaum, "Zur Kristallchemie von Titan-Legierungen", Naturwissenshaften, (1939), 27, p.674.