THE STRUCTURE OF N18

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Abstract

The structural relationships that control the behavior of the disk alloy N18, in current use at SNECMA, were studied. The alloy, in the fully heat-treated condition, contains three sizes of gamma prime. The largest, 4.3µm diameter, termed primary, forms during forging. The secondary, 0.2 µm, that forms during cooling exhibits a high sensitivity to cooling The finest, 0.02 mm, that forms during aging, and termed tertiary, appears to control properties. Extraction of the gamma prime phases, and their separation, allowed their individual chemical and x-ray analysis. Based on the extracted weight, the total gamma prime content of all three gamma prime forms is about 60 vol.%. The three forms of gamma prime were extracted and each was found to possess a different chemistry and lattice parameter. All forms exhibited a negative mismatch to the matrix, varying from -0.23% for the primary form to -0.38% of the tertiary. The chemistry of the gamma prime varied in such a manner that the Al, Ti and Co level decreased and the Cr and Mo level increased as the particle size i.e. temperature of formation of that particular gamma prime form, decreased. The effect of temperature on the amount of primary gamma prime and the effect of cooling rate on the particle size of the secondary gamma prime were quantified using image analysis. Cooling rate was found to have no effect on grain boundary curvature. On prolonged exposure above 650°C, the N18 alloy precipitates grain boundary sigma phase, tetragonal a = 0.8906nm and 0.4610nm with a (Ni, Co) (Cr, Mo) chemistry and, subsequently, m μ phase (rhombohedral, a = 0.4746nm, c = 2.5540nm) with a high Cr and high Mo content. The formation of these topologically close-packed phases is associated with the solution of the $0.02\mu m$, aging, gamma prime and a reduction in properties.

It is believed that the excellent properties of this alloy in the $650\,^{\circ}\text{C}$ region, and the very good hold time fatigue properties, which it exhibits, are due to the presence of the 0.02 μm gamma prime and a gamma matrix high in Cr, Co and Mo.

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Introduction

N18 is an advanced nickel base, gamma prime strengthened disk alloy. It was developed by SNECMA⁽¹⁾ as a powder metallurgy alloy, for service up to (700°C). The chemistry of N18 was evolved from Astroloy so as to achieve a low crack growth rate at 700°C, combined with good creep resistance and a high yield strength. N18 is heat treated for 4 hrs. 1165°C, delayed oil quench, typically with a 60 sec. delay time plus 12 sec. transfer time, followed by aging for 24 hrs. at 700°C and 4 hrs. at 800°C. Currently N18 is being used for compressor and turbine disks of the SNECMA M88 engine for the new Rafale fighter.⁽²⁾

Experimental

All of the work in this study was performed on a M88 HPT disk that was forged from a 22.8cm diameter extrusion of consolidated -200 mesh powder. The ASTM grain size of the examined material was in the range of 10 to 11 and the chemistry of the finished forging was: Co - 15.64%, Cr - 11.18%, Mo - 6.49%, Al - 4.37%, Ti - 4.36%, Hf - 0.50%, C - 0.018%, B - 0.015%, Zr - 0.030%, Fe - 0.13%, P - 0.004%, S - 0.002%, O - 0.075% and N - 0.013%. The study consisted of four stages: a structural analysis of the as-received disk, a study of the response of this alloy to heat treatment, and the determination of the effect of long time exposure. Standard extraction, (3) x-ray diffraction, AEM and $SEM^{(4)}$ examination procedures were used.

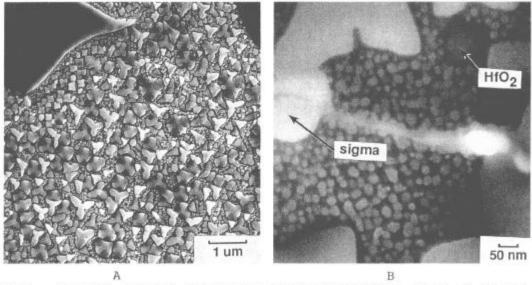


Figure 1. As Heat Treated structure illustrating three sizes of γ' (A) and minor sigma and Hf0₂ phases (B). SEM metholic HCl0₄ preparation.

Analysis of Fully Heat Treated Structures

Figure 1 illustrates the microstructure of as heat treated N18. The alloy contains three sizes of gamma prime, which will, for the sake of brevity, be defined as: Primary, with a particle size of 4.3 \pm 1.8 μm , this constituent is formed during the sub-solvus working and annealing of the alloy. Secondary, typically 0.21 \pm 0.08 μm diameter, it is the predominant morphology and forms largely on cooling from the 4 hours at 1165°C heat treatment. The secondary γ' can exhibit variable morphologies, depending on cooling rate. Tertiary gamma prime is the smallest (0.02 μm) and forms primarily on isothermal aging. It is always spherical and, because of its small particle size and resultant low strain

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energy, probably coherent with the matrix. The tertiary Y´ is usually present in higher concentrations at structural interfaces, i.e. grain boundaries and around primary gamma prime particles.

TEM, backed up by electron diffraction and x-ray energy dispersive analysis, as well as x-ray diffraction were used to study the minor phases present in as-heated treated N18. Electron diffraction of in-situ phases performed during TEM examination identified small amounts of a grain boundary faulted sigma phase (a=0.90nm, c=0.465nm) and an intradendritic, spherical, $\rm HfO_2$, usually some 0.10 μm diameter.

In order to determine the chemistry and structure of the Y phases, they were extracted in the standard 1% citric acid + 1% ammonium persulfate aqueous electrolyte and separated into three size fractions by a process that combined settling, and for very fine particles, centrifuging from a suspension in methyl alcohol complexed with 0.1% Triton. The effectiveness of the separation was judged by SEM examination which, as shown below, indicated an almost perfect separation of the three size fractions.

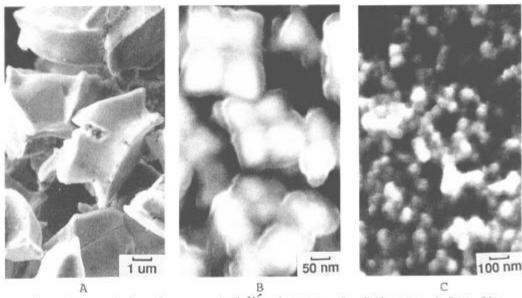


Figure 2. Extracted and separated Y phases. A. Primary, 4.3 μ m dia. a=0.35894nm, B. Secondary 0.21 μ m dia. a=0.35873nm, C. Tertiary 0.02 μ m dia. a = 0.35841.

X-ray diffraction analyses indicated a variation in lattice parameter ranging from a = 3.5894nm for the coarsest fraction, which consisted almost totally of the primary Y´, to 0.35873nm for the fraction which consisted of the cooling, secondary Y´, and 0.35839nm for the finest, tertiary, 0.02 µm diameter gamma prime. The extraction of the finest size was repeated and this time the measured lattice parameter was 0.35843nm within 0.01% of the first determination. The lattice parameter of the matrix was 0.35980nm, indicating that all three gamma prime sizes exhibited a negative mismatch to the matrix, the degree of mismatch being -0.23% for the primary fraction and -0.38% for the tertiary. It is still, however, likely that the tertiary, aging, constituent is coherent with the matrix. These results are given in Table I. It is possible to add that the diffraction peaks of the tertiary gamma prime exhibited the line

broadening expected from particles smaller than 100nm. When the peak width at half maximum height was used to calculate the crystallite size from the Scherrer formula, values of 0.02 mm, in complete agreement with the measured particle size, were obtained. As shown in Table I, the chemistry of the extracted gamma prime did vary. As the particle size decreased, which really means that the average temperature at which the gamma prime formed decreased, the lattice parameter decrease was associated with a lower Co, Ti, and Hf content, and a higher Cr and Mo level. Energy dispersive x-ray analyses of the same extractions that were used for x-ray diffraction verified these trends in a qualitative manner. The analysis of the gamma matrix, which was obtained by analyzing the electrolyte liquor, after extracting the gamma prime indicates a high Cr, (22.5 wt%), Co (25.0 wt%), and Mo (11.0 wt%) content. Additional extractions were performed under conditions where no separation of the different sizes of Y' was attempted. In triplicate determinations, these allowed the finding that N18 contains 58.2% gamma prime by wt%, or 60.8 vol%. The partitioning of this total to the three different forms given in Table I is based on image analysis, which showed that primary Y' occupied 22.6% of the area, secondary 45.0 and tertiary 13.7%. Due to the excellent depth of a field emission SEM, as well as the lack of complete flatness (RMS=0.06µm) in specimens electropolished in metholic perchloric, the image analysis results can never be completely accurate, and thus this is an approximation.

Table I

Characteristics of Gamma and Gamma Prime in As Heat-Treated N-18

Phase	Particle Size µm						_	•	Ti	Hf
Primary γ	4.3 ± 1.8	17	0.35894	64.2	9.0	2.9	1.3	13.1	9.1	0.4
Secondary Y	0.21 ± 0.0	08 34	0.35873	65.0	7.6	2.4	1.7	14.4	8.7	0.2
Tertiary γ´	0.02 ± 0.0	01 10	0.35843	65.3	6.9	4.5	2.6	14.1	6.6	0.1
Gamma	-	39	0.35980	39.3	24.8	25.3	6.7	3.1	0.6	0

Formation of Gamma Prime

The three sizes of gamma prime form by three different processes. Each was studied in turn. The amount of primary γ' that is retained after forging reflects both the processing and annealing temperatures. To study the relationship between temperature, and amount of γ' , 0.6 x 0.6 x 0.3cm specimens were exposed in the temperature range of 1000 to 1200°C for 1 hour and water quenched. The amount of γ' was determined by point counting as a function of temperature and the data could be fitted to the following equation:

% Υ by volume = 517.65 - 0.43460 (°C) (R²=0.994). (1).

The high slope of this relationship should be noted. The control of the primary gamma prime is an important factor in achieving optimum properties in LCF. Examination of failed LCF specimens often identified the boundary between two adjoining primary γ^{\prime} particles as a preferred site for crack nucleation.

The precipitation of the cooling, secondary gamma prime was studied by spot welding a thermocouple to the center of a $1.3 \times 1.3 \times 0.6$ cm specimen equilibrating it for 1 hour at 1177° C, and cooling it at a rate of that varied from 555 to 30° C/min. to 870° C, followed by water quenching.

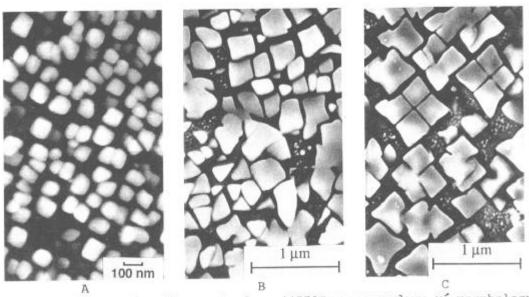


Figure 3. Effect of cooling rate from 1177°C on secondary γ' morphology. A. 550°C/min. B. 100°C/min. C. 30°C/min.

The effect of cooling rate on the secondary, cooling forms of Υ , (Figure 3) produced small (0.05µm) equiax particles at 555°C/min. (Figure 3A) to cuboidal at 216°C/min, with increasing tendency to develop an ogdoadial morphology at even slower cooling rates, that becomes quite pronounced at 30°C/min. (Figure 3C) when the average secondary gamma prime phase had an average diameter of 0.60 \pm 0.13µm. Increasing the cooling rate increases the hardness of the as cooled alloy per the following relationship: Rc=32.284 + 4.9747x10^-2 (d°C/dt) - 5.4420x10^-5 (d°C/dt)^2, (R²=0.991) (2) Figure 4 shows that the relationship between cooling rate (d°C/dt) and the diameter (D) of the cooling Υ in microns can be expressed as:

log D = 0.257 - 1.97 x 10⁻³ (d°C/dt) , (R²=0.95) (3) Examination of Figures 3B and C indicates the presence of a very fine γ' which is believed to have formed on "cooling" after water quenching. This fine gamma prime is termed tertiary in Figure 4. It is believed that this fine γ' (\leq 0.02 μ m) formed at about 700-870°C, essentially on or after water quenching. All the variations of cooling rate, studied here, appeared to have no effect on the volume of the γ' that formed on cooling. The extent to which variations in cooling rate can effect mechanical properties is appreciable and is suggested by the hardness relationship given in Equation 2.

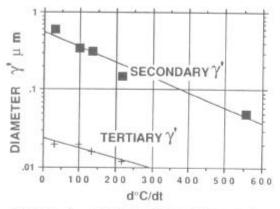


Figure 4. Effect of cooling rate from 1177°C to 870°C on Y size.

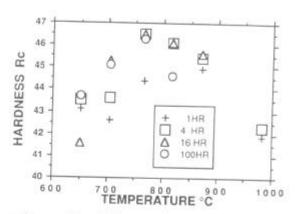


Figure 5. Effect of aging for 1 to 100 hrs. on material oil quenched (555°C/min) from 1166°C. Note max Rc after 4 hrs. 766°C.

In some alloys, variation in cooling rate can effect the curvature of the grain boundaries. This effect was studied by examining the triple points of samples electropolished and etched in metholic HCl and measuring the ratio of actual grain boundary length to the equivalent straight line distance, at a triple point (x25,000) thus calculating the grain boundary curvature ratio (GBCR). For N18 the GBCR was 1.05 at a cooling rate of 216°C/min, 1.10 at 133°C/min., 1.06 at 100°C/min, and 1.05 at 30°C/min. Essentially this alloy's grain boundary morphology is not sensitive to cooling rate.

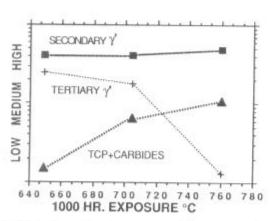


Figure 6. On exposure, the amount of tertiary Y decreases rapidly above 700°C, while the amount of TCP phases (sigma, and later mu) increases.

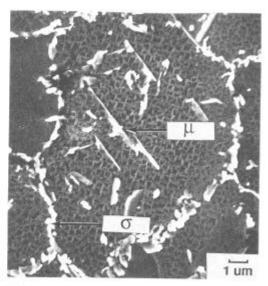


Figure 7 After 1000 hr. exposure at 760°C, copious grain boundary sigma and intragranular mu phase are present.

The nature of the aging reactions in N18 was studied by exposing samples previously oil quenched (555°C/min.) from 1160°C to aging for 1 hr. to 100 hrs. over the temperature range of 650 to 982°C. As shown in Figure 3C the as oil quenched specimens, which exhibited a hardness of Rc=43.1, possessed some 40 vol % of a 0.073 μ m Y´. Figure 5 illustrates the effect of aging on Rc, documenting maximum hardening within 4 hrs. at 766°C. Overaging, at least on the basis of Rc, initiates within 100 hrs. at 816°C. The hardening response on aging could be associated with the formation of an aging Y´ that was coherent and <0.02 μ m in diameter (See Figure 1).

Long Time Stability

Test coupons were exposed for up to 1000 hrs. at 650,704, and 766° C. In addition, a number of stress rupture specimens which had been tested in this temperature range, were examined. The presence of stress, however made no major difference in the results. All specimens that exhibited a major structural change were characterized. X-ray diffraction of residues from 90% CH_3OH - 10% HCl extractions, backed by AEM procedures, including electron diffraction and x-ray energy dispersive analysis were used to identify any new phases. An approximate quantification of the precipitation reactions based on image analysis, is presented in Figure 6, while Figure 7 illustrates the structure after 1,000 hrs./766°C.

At 650°C, with the exception of continued precipitation of tertiary γ' few changes in structure occurred. Small amounts of grain boundary MagCa (a=1.06nm) were found after 1000 hr. at 650°C and in one stress rupture specimen, tested at 650°C/930MPa/1100hr., an increase in sigma phase was observed. At 704°C, the amount of the ultra fine tertiary Y decreased, At 766°C the amount of grain boundary sigma and more sigma formed. continued to increase even more rapidly. After 100 hrs. exposure at 766°C, very little tertiary gamma prime was left, and after 1000 hrs., small amounts of intragranular mu phase (rhombohedral a = 0.4746nm, c = 2.5540nm) were present. X-ray, energy dispersive analysis of the extracted mu phase indicated a chemistry of 14.8% Ni, 28.2% Co, 37.4% Cr, 0.6% Ti, and 18.8% Mo, all in atomic %. In most cases, the lattice parameters of the tetragonal sigma were a = 0.8906nm, c = 0.4610nm, with a chemistry of 18.5% Ni, 30.6% Co, 40.5% Cr, 1.1% Ti, and 9.3% Mo, also in atomic %.

The main structural reactions of alloy N18 are summarized in Figure 8.

DISCUSSION

In general, the lattice parameter of the Υ in alloy N18 decreases with the decreasing particle size or decreasing temperature of formation. Decreasing lattice parameter is associated with decreasing Co, Ti, and Hf content and increasing Mo and Cr levels. All three gamma prime sizes exhibit negative misfit, ranging from -0.23% for the primary gamma prime that formed by subsolvus working and annealing, to -0.30% for the secondary, cooling, gamma prime, and -0.38% for the tertiary, finest, gamma prime.

The high Cr and Mo content of the austenitic matrix, which analyzed some 40.0 wt% Ni, 25.0 wt% Co, 22.5 wt% Cr, 11.0 wt% Mo, 1.45 wt% Al and 0.5

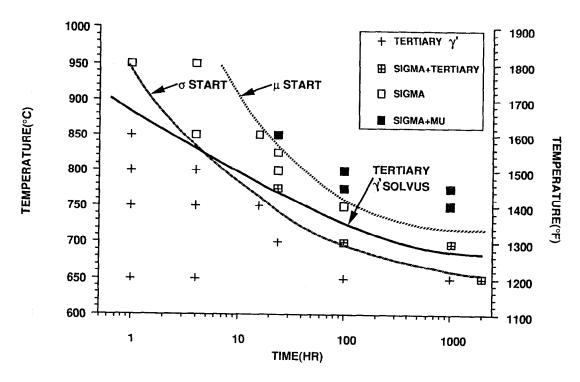


Figure 8. Plot of stability for the critical phases in N18 alloy. Under all conditions given above, the primary and secondary forms of gamma prime, $\rm Hf0_2$ and the small amount of sigma that forms on cooling would also be present. The critical 0.02 μ m, tertiary gamma prime that forms in 1 hr. at 870°C, up to 16 hrs. at 760°C, and up to 1,000 hrs. at 649°C is associated with optimum properties. As the Cr and Mo containing tertiary gamma prime dissolves, grain boundary sigma phase and, later, intragranular Mu phase form.

wt% Ti, should also be noted. The analyses of the matrix and Y phases appear reasonable. As they were obtained on the same samples as were subjected to SEM examination (See Figure 2) and x-ray diffraction analyses, a high cleanliness of separation can be claimed. It is possible, however, that some fraction of the phases was dissolved in the extraction process. The analyses are within the known solubilities in gamma prime (5), and compare reasonably with earlier published values for similar alloys, such as Udimet 700(6). The sum of Ti, Al and Hf for each particle size of gamma prime is just under 25 at%, suggesting that all of the Mo and at least some of the Cr are also occupying the cube corner positions, while Co and possibly some of the Cr join the Ni atoms in the face centered sites. Each of the gamma prime structures forms under completely different conditions, accounting for the varying gamma prime chemistry and lattice parameter.

The large primary particles form during forging and annealing, well below the Υ solvus. Reference to equation indicates, that due to the steepness of the solvus, the control of the primary Υ may be difficult. The amount of primary gamma prime changes by 2.4 vol% for every 1°C change in finishing temperature. The processing "window" for control of primary is therefore small. Since the amount of primary Υ was some 17 vol%

Equation 1 indicates that the forging studied here was annealed at 1152°C, in fair agreement with the specified 1165°C annealing temperature. The extrapolation of Equation 1 indicates a Y´ solvus of 1191°C, in agreement with the reported value (1). Control of the amount of gamma prime is important for two reasons. Obviously, alloying elements that partition to this phase contribute little to strength, except that the presence of this constituent allows easier grain size control during processing. Secondly, points of contact between primary gamma prime, a morphological feature that will increase with the amount and uniformity of distribution of the primary gamma prime, are areas of preferential crack nucleation in fatigue.

No quenching rate can suppress the formation of secondary gamma prime on cooling. This constituent forms largely during cooling above 870°C. Even cooling rates as rapid as 555°C/min. do not suppress the formation of secondary gamma prime. The relationship between cooling rate and resultant gamma prime size is shown in Figure 4. The forging supplied by SNECMA for this study exhibited a secondary gamma prime size of some 0.2 µm, suggesting a cooling rate of approximately 200°C/min. could probably not be achieved in very thick sections. between secondary gamma prime size and properties is not known for this alloy, but some decrement should be expected, particularly for elevated temperature yield and creep, at least for secondary gamma prime sizes much above 0.3 to 0.4 mm. This is partially documented by the effect on hardness expressed in Equation 2. The cooling rate does not appear to affect the amount of gamma prime, nor does the cooling rate produce any change in the straightness of the grain boundaries. In N18 the grain boundaries are always essentially straight. This is probably due to the subsolvus annealing conditions and the resultant large amount of primary gamma prime present. This phase pins the grain boundaries very effectively and restricts any grain boundary bowing. The good hold time fatique properties of this alloy(1) do not support the hypothesis that wavy or serrated grain boundaries (7) are absolutely critical to good hold time fatique properties. The finest $(0.02\mu m)$, tertiary, gamma prime forms largely on aging, although some can form on cooling through the aging range (650-875°C). Although the studies performed here were on specimens oil quenched from 1166°C, an artificial condition in terms of the heat treatment of a forging, the maximum rate of hardening was observed to have occurred at 766°C and optimum hardness was achieved in 4 hrs. The SNECMA recommended heat treatment of 24 hrs. at 700°C + 4 hrs. at 800°C is a reasonable one, fully capable of achieving optimum properties. initial 24 hrs. at 700°C cycle may, however, not be required, but more experimentation would be necessary to confirm this possibility. tertiary gamma prime tends to form in highest concentrations in areas that are slightly denuded of secondary gamma prime, particularly grain boundaries. This tendency, as well as its coherent nature, suggested by its spherical form, and very small size (0.02 µm) explain why this phase has a large effect on the properties of alloy N18.

The high Cr and Co level of the matrix solid solution suggest a matrix of low stacking fault energy with sufficient cobalt and chromium to alleviate any major contribution of the 0_2 embrithement (a) stress-assisted grain boundary oxidation (SAGBO) which may well dictate the rate of crack propagation in fatigue, and particularly, hold time fatigue conditions. The beneficial effects of Cr level on the fatigue crack growth rate in Inconel alloy 718 has been well documented (b), and cobalt base alloys do

not suffer from the SAGBO phenomenon (8). The effect of exposure on structural relationships is summarized in Figure 8. Additional grain boundary sigma (tetragonal, a = 0.890nm, c = 0.4610nm) with a (Ni Co) (Cr Mo) chemistry forms on exposure above 650°C. This is followed by the solution of the ultrafine 0.02 µm gamma prime. Subsequently, at least above 700°C, mu phase begins to form, largely intragranularly. The mu phase is rhombohedral (a = 0.4746nm, c = 2.554nm) and high in both Mo and Cr. The effect of exposure on the size and amount of the various phases is given in Figure 6. The rapid reduction in fine gamma prime, rather than a growth in gamma prime, particularly above 700°C, and the increase in TCP phases, above 650°C should be noted. Precipitation of high Cr and high Mo, sigma and mu phases will, of course, deplete the matrix of these elements, but being non-continuous may not be embrittling. It is likely that the solution of the high Cr and Mo tertiary gamma prime and the precipitation of mu and sigma phases are related.

This structural examination suggests that the excellent properties of N18 are associated with the presence of the ultrafine, aging gamma prime whose solution dictates the useful temperature maximum for this alloy. In addition, the high chromium cobalt and molybdenium content of the matrix may be responsible for the good hold time fatigue behavior of this composition. However, mechanical evaluations must be relied on as the final arbiter of alloy properties. The processing of N18 appears to require good control of working temperatures. The slope of the Y' solvus is unusually steep and the size of the cooling gamma prime is fairly sensitive to the cooling rate.

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