APFIM/TEM CHARACTERIZATION OF PRECIPITATION IN ALLOY 718

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Abstract - The combined techniques of atom probe field-ion microscopy and transmission electron microscopy have been used to characterize the microstructure of Alloy 718, a γ'' and γ' strengthened nickel-base superalloy. The effect of heat treatment on precipitation has been studied. The morphology, crystal structure, and distribution of the phases have been identified by transmission electron microscopy and the chemistries of the γ'' and γ' precipitates have been measured with the atom probe. The results show a wide variation in the composition of these precipitates which is dependent upon aging treatment.

INTRODUCTION

A widely used commercial superalloy for gas turbine and related applications is the niobium-modified nickel-base Alloy 718. These applications require materials with good mechanical properties and microstructural stability at temperatures up to 650°C. These properties are achieved as a result of a four stage thermal treatment during which a complex multiphase microstructure is developed. Several time-temperature-transformation (TTT) diagrams exist which are frequently used to predict the phases formed during these thermal treatments.^[1-3] The primary strengthening precipitate in this alloy is a $D0_{22}$ -ordered γ'' phase, although an $L1_2$ -ordered γ' phase is also present.^[2,9] The body-centered tetragonal γ'' phase is coherent with the face-centered cubic γ matrix, and exhibits the following orientation relationship: $(001)_{\gamma''} \parallel \{001\}_{\gamma}$ and $[100]_{\gamma''} \parallel \langle 100 \rangle_{\gamma}$.^[4-6] Other phases which have been reported to form in Alloy 718 include orthorhombic $D0_4$ -ordered δ (Ni_3Nb), Laves, and MC-type carbides.^[1,2,6] The δ forms along grain boundaries and within the γ matrix after prolonged aging. The plate-like δ is crystallographically related to the γ by the orientation relationship: $(010)_{\delta} \parallel \{111\}_{\gamma}$ and $[100]_{\delta} \parallel \langle 110 \rangle_{\gamma}$.^[5] Delta precipitation is reported to occur during the overaging of the γ' precipitates, and the presence of the plate-like δ is generally deleterious to the mechanical properties of the alloy.^[2,8,9] Although numerous microstructural studies have been conducted on Alloy 718,^[1-9] the chemistry of these coexisting phases has not been accurately established.

In this study, atom probe field-ion microscopy (APFIM) and transmission electron microscopy (TEM) have been used to characterize the microstructure of Alloy 718 after selected aging treatments. Previously, APFIM has been successfully applied to the evaluation of several nickel-base superalloys including IN939,^[10] RSR 143,^[11] U720,^[12] CMSX2,^[13] Nimonic PE 16,^[14] and SRR 99.^[15]

MATERIALS AND EXPERIMENTAL TECHNIQUES

The nominal bulk composition of Alloy 718 studied in this investigation is shown in Table 1. The alloy was characterized after two 4-stage heat treatments: (A) 1h at 1038°C, 8h at 871°C, 8h at 760°C, and 8h at 649°C; and (B) 1h at 1038°C, 8h at 982°C, 8h at 760°C, and 8h at 649°C. The material was fast air-cooled to room temperature between each stage. These two heat treatments differ in only the temperature of the second stage.

Specimens for TEM characterization were prepared with a conventional jet polishing technique and subsequently examined in a Philips EM400T analytical electron microscope operated at 120 kV. All APFIM studies were performed with the ORNL energy-compensated atom probe.^[16] All compositions are presented in atomic percent. All field-ion micrographs were obtained at 50K with neon as the imaging gas.

MICROSTRUCTURE

(A) 1h at 1038°C, 8h at 871°C, 8h at 760°C, and 8h at 649°C

The presence of extensive intergranular and intragranular precipitation was revealed by TEM examination, as shown in Fig. 1. Globular ($\sim 1 \mu m$) and plate-like (~ 1 to $8 \mu m$) precipitates were identified by electron diffraction as Ni_3Nb (δ). The globular δ precipitates were located exclusively at grain boundaries, whereas the plate-like precipitates were located both at grain boundaries and within the grain. The nature and extent of intragranular precipitation is shown in Fig. 2. Thermal treatment A resulted in a relatively

uniform distribution of coarse primary γ'' that was $\sim 0.3 \mu\text{m}$ in length. In addition, fine 10-20 nm γ' and secondary γ'' precipitates were detected throughout the matrix. A zone denuded of γ'' was observed around all δ and primary γ'' precipitates. Detailed examination of the microstructure in the vicinity of the intergranular δ precipitates revealed an approximately 0.4- μm -zone devoid of secondary γ'' and a more extensive region where no primary γ'' was observed.

Both coarse and fine brightly-imaging precipitates were observed in the field-ion image, Fig. 3. The coarse precipitates were elongated in shape, whereas the fine particles were roughly spheroidal. It was inferred that the coarse precipitates were primary γ'' since their sizes were similar to those of the primary γ'' measured in the TEM; atom probe selected area analysis confirmed this interpretation. The size of the fine precipitates was in agreement with the TEM observations of the γ' and secondary γ'' .

(B) 1h at 1038°C, 8h at 982°C, 8h at 760°C, and 8h at 649°C

The microstructure of the alloy after this aging treatment was characterized by matrix precipitation of γ'' and γ' . A TEM image (formed with both γ'' and γ' superlattice reflections) in Fig. 4 clearly shows two (100) variants of the γ'' precipitates. Fine γ' precipitates appear as faint, roughly spheroidal particles in the matrix. The amount of γ'' is significantly greater than that of γ' and the sizes of both phases are between 10 and 40 nm in length. Precipitates of γ'' were also present on some grain boundaries and were somewhat coarser than their matrix counterparts, Fig. 5. Several coarse ($\sim 3 \mu\text{m}$) lenticular δ precipitates were observed at grain boundaries and within the matrix. A narrow zone denuded of γ'' , ~ 100 nm in width, was occasionally detected near the δ precipitates. Other coarse microstructural features included blocky Nb-rich MC-type carbides approximately 0.5 μm in size. The morphology and distribution of these carbides suggests that they had formed at an earlier stage during thermomechanical processing, and were not dissolved during the 1038°C homogenization anneal.

Field-ion images of the alloy after aging condition B showed a high number density of brightly-imaging precipitates in the dark γ matrix, Fig. 6. The size of these precipitates was consistent with the TEM observation for the γ'' and γ' precipitates; however, since all the precipitates exhibited the same contrast in the field-ion micrograph, their type could not be determined from the image.

MICROCHEMISTRY

(A) 1h at 1038°C, 8h at 871°C, 8h at 760°C, and 8h at 649°C

Selected area atom probe analyses of the primary γ'' precipitates revealed a complex partitioning of the elements as shown in Table 2. The average composition of three of these precipitates revealed that Nb and Ti were enriched in the precipitates and that Al, Fe, Cr, Si, and Mo were depleted.

Atom probe selected area analysis of the fine precipitates revealed a wide variation in composition (e.g. Nb contents from 7 to 16%, Ti contents from 6.6 to 11.4%, and Al contents from 2.7 to 13.3%). The normal method that is used to identify the type of precipitate from atom probe data is from its composition. However, both γ'' and γ' have been described as $\text{Ni}_3(\text{Nb}, \text{Al}, \text{Ti})$ with unspecified variations in Nb, Al and Ti contents. In order to ascribe a structural type to the individual precipitates, the atom probe data were analyzed in terms of the ratios of Al, Ti, and Nb {i.e. $\text{Al}/(\text{Al}+\text{Ti}+\text{Nb})$, $\text{Ti}/(\text{Al}+\text{Ti}+\text{Nb})$, and $\text{Nb}/(\text{Al}+\text{Ti}+\text{Nb})$ }. A graphical representation of these data, sorted in increasing niobium ratio, for 15 fine precipitates and a primary γ'' (#16) is shown in Fig. 7. The primary γ'' precipitate was found to be rich in Nb and strongly depleted in Al. It is reasonable to presume a similar trend for the fine γ'' . Examination of the ratios in Fig. 7 reveals that a division based on this trend is viable and that precipitates 9 through 15 could be assigned to γ'' and 1 through 8 to γ' . However, the Al levels of the fine γ'' precipitates are a factor of 10 higher than the primary γ'' , and conversely, the Nb levels are approximately 50% lower. The full chemistries of several fine precipitates, classified by this criterion, are listed in Tables 3 and 4. Elements other than Nb and Al do not appear to have a strong preference between the γ' and γ'' .

Atom probe analyses revealed that the γ matrix is significantly depleted in Nb, Al, and Ti with respect to the nominal bulk chemistry and to the precipitates. The full composition of the γ matrix is given in Table 1. As expected, the levels of Fe, Cr, Mo and Si are significantly higher than in the precipitates.

(B) 1h at 1038°C, 8h at 982°C, 8h at 760°C, and 8h at 649°C

The compositions of the intragranular precipitates and matrix were measured by selected area atom probe analysis. A similar procedure to that described above was used to determine the identity of the precipitates. The relative abundances of Nb, Al and Ti are presented in graphical form in Fig. 8. Two distinct composition categories are evident. Precipitates 1 through 8 were enriched in Al and depleted in Nb in contrast to precipitates 9 through 16 which were enriched in Nb and depleted in Al. Tables 5 and 6 show

that the γ' contains approximately 10.3% Nb, whereas the γ'' precipitates are richer in Nb ($\sim 23\%$). Other significant differences lie in the relative Al and Ti contents of the precipitates: γ' is enriched in both Al (8.1%) and Ti (7.8%) as compared with 1.2% Al and 5.4% Ti in γ'' .

Atom probe analysis of the γ matrix again revealed the extent of solute depletion which accompanies γ'' and γ' precipitation. The composition of the γ matrix as measured by the atom probe is listed in Table 1. The matrix is enriched in Fe, Mo and Si, but significantly depleted of Nb, Al and Ti.

Comparison of the heat treatments

The results indicate that the microchemistry of the precipitates depends significantly on the heat treatment. All precipitates were enriched in Nb and Ti and, except for the primary γ'' , were enriched in Al. The Nb level of the γ'' after heat treatment B is similar to that of the primary γ'' precipitates formed during treatment A. In contrast, the secondary γ'' (treatment A) contained approximately half as much Nb, but increased levels of both Ti and Al. Smaller differences were observed between the γ' precipitates. In these precipitates, the Nb level was slightly lower and the Al and Ti contents were higher after heat treatment A.

Only minor differences were found in the matrix compositions of the two heat treatments. In both cases, the matrix was depleted in Nb, Al and Ti, although significant levels remained in solution.

SUMMARY

Distinctly different microstructures were produced as a result of changing the second stage aging temperature. Aging at 871°C promotes the formation of coarse δ Ni_3Nb precipitates both at grain boundaries and within the matrix. Precipitation and coarsening of γ'' occurs during this stage. Aging at 982°C eliminates the widespread precipitation of δ and coarse γ'' ; the only δ precipitates detected were sparsely distributed. Subsequent stages of the thermal treatments produce the fine distribution of both γ'' and γ' precipitates throughout the γ matrix. The microchemistry of the precipitates showed wide variability in Nb, Ti, and Al contents. In addition, the results demonstrate that existing time-temperature-transformation diagrams do not correctly reflect the microstructure produced during these multi-stage thermal treatments.

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Fig. 1. TEM micrographs showing globular and plate-like δ precipitates formed during thermal treatment A. Note the presence of coarse primary γ'' and a denuded zone near the grain boundary.

Fig. 2. (a) Intragranular precipitation of primary and secondary γ'' ; (b) (100)_s dark field TEM micrograph of primary and secondary γ'' , and γ' (arrowed) formed during thermal treatment A.

Fig. 3. FIM micrograph of primary γ'' and fine γ' after heat treatment A.

Fig. 4. (110)_s dark-field TEM image of γ'' and γ' in Alloy 718 after thermal treatment B.

Fig. 5. Dark-field TEM micrograph of intergranular γ' after treatment B.

Fig. 6. Field-ion micrograph of fine γ and γ' formed during thermal treatment B.

Fig. 7. Relative proportions of Al, Ti, and Nb in the precipitates after heat treatment A.

Fig. 8. Relative proportions of Al, Ti, and Nb in the precipitates after heat treatment B.

Table 1. Comparison of the compositions of the γ matrix.

	Nb	Al	Ti	Fe	Cr	Co	Mo	Mn	Si
Bulk	3.2	0.95	1.15	20.3	21.6	0.26	1.81	0.17	0.43
A	1.69	0.50	0.50	25.5	17.4	0.26	2.32	0.15	0.60
B	1.69	0.44	0.34	23.3	21.7	0.24	2.14	0.12	0.63

A = 1 h 1038°C, 8 h 871°C, 8 h 760°C, 8 h 649°C. B = 1 h 1038°C, 8 h 982°C, 8 h 760°C, 8 h 649°C.

Table 2. Atom probe analysis of primary γ'' precipitates aged 1 h at 1038°C, 8 h at 871°C, 8 h at 760°C, 8 h at 648°C, (A).*

	Nb	Al	Ti	Fe	Cr	Co	Mo	Mn	Si
1	22.6	0.51	7.35	1.19	0.57	0.08	0.74	1.19	0.04
2	21.6	0.39	5.01	0.96	0.96	0.66	1.27		0.08
3	23.0	0.67	4.42	1.10	0.70	0.07	1.26	0.07	0.10
Avg.	22.4	0.52	5.59	1.08	0.74	0.27	1.09	0.42	0.07

Table 3. Atom probe analysis of secondary γ'' precipitates aged 1 h at 1038°C, 8 h at 871°C, 8 h at 760°C, 8 h at 649°C, (A).*

	Nb	Al	Ti	Fe	Cr	Co	Mo	Mn	Si
1	13.0	6.66	7.08	1.90	0.63	0.21	0.74		
2	15.9	6.95	9.93	2.23	0.25				
3	9.81	5.49	10.3	1.27	0.92		0.20	0.10	
4	9.63	7.29	6.52	2.25	0.46	0.17	0.17	0.10	0.10
5	11.0	2.69	7.32	1.89	1.05	0.10	0.15	0.15	
6	9.99	5.10	11.4	2.04	0.31	0.10	0.10	0.20	0.31
7	14.9	5.39	7.10	4.28	2.20	0.12	0.49	0.12	0.12
Avg.	12.0	5.65	8.52	2.27	0.83	0.10	0.26	0.10	0.07

Table 4. Atom probe analysis of γ' precipitates aged 1 h at 1038°C, 8 h at 871°C, 8 h at 760°C, 8 h at 649°C, (A).*

	Nb	Al	Ti	Fe	Cr	Co	Mo	Mn	Si
1	8.72	8.81	10.2	2.16	0.31	0.09	0.09	0.13	0.31
2	8.26	10.3	7.34	1.84	0.84	0.08	0.08	0.38	0.22
3	8.27	10.2	8.08	1.47	0.92		0.14		0.18
4	7.09	10.8	7.98	1.33	0.29	0.29		0.44	0.44
5	7.10	9.20	8.01	1.29	0.29	0.14		0.14	0.09
6	8.09	9.62	8.49	2.25	0.21	0.15	0.21	0.06	0.15
7	8.00	8.88	6.61	1.66	0.20	0.10	0.18	0.21	0.14
8	8.40	9.10	9.78	1.52	0.24	0.07	0.07	0.24	0.13
9	8.39	13.3	7.10	1.72	0.43	0.80	0.21	0.65	0.43
10	7.77	10.2	9.20	2.05	0.61	0.41	0.20	0.20	0.61
11	8.41	10.5	7.84	2.56	0.85	0.14	0.28		0.14
12	8.56	11.4	7.74	2.65	0.10	0.41	0.31		0.31
13	8.63	8.94	8.38	1.63	0.30	0.25	0.41	0.15	0.10
14	10.2	9.82	9.61	1.64	0.27	0.20	0.27	0.34	0.34
15	9.02	11.5	11.0	1.00	0.25	0.50	0.50	0.50	
16	8.00	10.1	8.72	1.87	0.42	0.21	0.21	0.10	0.31
Avg.	8.31	10.2	8.51	1.79	0.41	0.24	0.20	0.22	0.24

Table 5. Atom probe analysis of γ' precipitates aged 1 h at 1038°C, 8 h at 982°C, 8 h at 760°C, 8 h at 649°C, (B).*

	Nb	Al	Ti	Fe	Cr	Co	Mo	Mn	Si
1	8.88	14.4	1.78	1.95	1.60	0.09	0.62	0.02	0.18
2	11.6	7.00	5.60	1.40	0.14				0.28
3	8.47	8.19	11.75	1.91	0.81	0.27	0.14	0.14	0.14
4	6.54	6.73	9.61	2.12			0.19	0.19	
5	10.9	7.50	10.1	1.77	0.14	0.14	0.40	0.14	0.14
6	12.9	6.71	8.86	1.65	0.63	0.25		0.25	0.38
7	13.4	8.36	5.00	1.35	0.29		0.47	0.06	0.12
8	9.51	5.83	9.38	4.69	3.29		0.89		0.63
Avg.	10.3	8.09	7.76	2.10	0.86	0.09	0.34	0.18	0.23

Table 6. Atom probe analysis of γ'' precipitates aged 1 h at 1038°C, 8 h at 982°C, 8 h at 760°C, 8 h at 649°C, (B).*

	Nb	Al	Ti	Fe	Cr	Co	Mo	Mn	Si
1	19.6	1.77	4.91	2.10	1.51	0.12	0.57		0.08
2	27.1	1.46	4.92	2.39	1.73	0.13	1.06	0.13	0.26
3	18.3	0.47	4.80	1.08	1.89	0.13	1.42	0.07	0.07
4	23.7	0.89	5.58	1.56	1.56	0.22	0.66		0.22
5	26.0	0.22	6.11	1.36	1.36		0.22		
6	24.0	1.21	6.25	2.01	0.81		0.40		0.20
7	18.8	3.40	6.30	2.83	2.08	0.06	1.07	0.12	0.12
8	27.0	0.73	4.40	1.92	1.28		1.74	0.09	0.09
Avg.	23.1	1.27	5.41	1.91	1.53	0.08	0.89	0.05	0.13

*The balance of these measurements is nickel; results quoted in atomic percent.