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Comparison of the phase compositions in Alloy 718 measured by atom probe tomography and predicted by thermodynamic calculations

M.K. Miller *, S.S. Babu, M.G. Burke [1]

Microscopy and Microanalytical Sciences Group, Metals and Ceramics Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6376, USA

Abstract

A comparison has been made of the phase compositions predicted by thermodynamic calculations and measured by atom probe tomography in a commercial Alloy 718 nickel based superalloy. The results indicate that caution should be taken in the application of the Ni–Fe database/Thermocalc™ to superalloys because some of the predicted phases may not correspond to actual microstructure of commercial alloys. When microstructural information is taken into account and absent phases are suppressed in the calculations, reasonable agreement between the atom probe data and the thermodynamic predictions may be achieved. Published by Elsevier Science B.V.

Keywords: Superalloy; Alloy 718; Atom probe; Alloy phase composition

1. Introduction

The design of new or modified nickel-based superalloys for high temperature applications is an extremely expensive and time consuming process. Therefore, thermodynamic calculations are being introduced in an attempt to reduce these costs. However, little experimental data are available on the effectiveness of these predictive tools in complex multiphase and multicomponent commercial alloys. The three-dimensional atom probe (3DAP) is able to determine the partitioning and concentrations of the alloying elements in the phases present in these complex systems [1].

In this study, thermodynamic predictions of the phase compositions [2] are compared to the compositions of the phases, as determined by atom probe tomography, at various annealing temperatures. The alloy selected for this study was a commercial Alloy 718 [3]. Niobium-containing Alloy 718 is strengthened by a combination of DO_{22}-ordered $Ni_3(Nb,Ti)$ γ'' and $Ni_3(Al,Ti,Nb)$ γ' phases in a face centered cubic γ matrix [3–7]. Previous atom probe tomography characterizations of Alloy 718 [8–10] revealed that the secondary or fine ($< \sim 20$ nm diameter) precipitates consisted of two distinct types of regions enriched in either niobium or in aluminum and titanium that are characteristic of the γ'' and γ' phases, respectively. This study complements a previous atom probe tomography study on another Alloy 718 with a different multistep heat treatment [10].

2. Experimental

The nominal composition of the commercial Alloy 718 used in this study was Ni—21.5 at.% Fe, 19.6% Cr, 0.31% Co, 1.76% Mo, 3.24% Nb, 1.18% Ti, 1.27% Al and 0.19% C (Ni—20.7 wt.% Fe, 17.6% Cr, 0.32% Co, 2.92% Mo, 5.21% Nb, 1.05% Ti, 0.55% Al, and 0.04% C). The material was given a multistep heat treatment of 1 h at 1093 °C, 8 h at 718 °C, a slow cool at a rate of 55 K h^{-1} to 621 °C, 8 h at 621 °C and an air cool to room temperature. The microstructural characterizations were performed after the step 8 h at 718 °C and after the complete multistep heat treatment.

* Corresponding author. Tel.: +1-865-574-4719; fax: +1-865-241-3650.

E-mail address: millermk@ornl.gov (M.K. Miller).

[1] Present address: Bechtel Bettis Inc., West Mifflin, PA 15122, USA.

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Table 1
Predicted compositions of the coexisting phases

Element	Bulk at.%	γ			γ″		γ′	
		1093 °C	718 °C	621 °C	718 °C	621 °C	718 °C	621 °C
Fe	21.47	21.56	26.45	27.93	1.09	0.70	3.64	2.95
Cr	19.61	19.69	23.75	22.86	0.56	0.31	0.80	0.52
Co	0.31	0.32	0.34	0.35	0.21	0.19	0.17	0.16
Mo	1.76	1.77	1.82	1.37	0.50	0.43	0.18	0.11
Nb	3.24	3.12	0.46	0.20	20.41	20.88	7.52	7.50
Ti	1.18	1.21	0.14	0.05	3.89	3.53	7.59	7.36
Al	1.27	1.19	0.38	0.21	0.20	0.17	8.43	8.71
Mole percent		99.61%	78.07%	72.09%	9.35%	10.70%	10.29%	11.60%
Element	Bulk at.%	NbC		$Cr_{23}C_6$	σ			
		1093 °C	718 °C	621 °C	718 °C	621 °C		
Ni	50.94	–	–	0.30	16.54	15.13		
Fe	21.47	–	–	1.55	18.66	19.36		
Cr	19.61	0.07	0.02	67.30	49.77	51.67		
Co	0.31	–	–	–	0.44	0.52		
Mo	1.76	0.16	0.23	10.15	14.59	13.32		
Nb	3.24	36.35	50.52	–	–	–		
Ti	1.18	17.20	3.23	–	–	–		
Al	1.27	–	–	–	–	–		
C	0.19	46.22	46.01	20.69	–	–		
Mole percent		0.39%	0.42%	0.93%	1.88%	4.67%		

The balance is nickel and the results are in atomic percent.

Table 2
Predicted compositions of the coexisting phases with the δ, σ, and Laves phases suppressed

Element	Bulk at.%	γ			γ″		γ′	
		1093 °C	718 °C	621 °C	718 °C	621 °C	718 °C	621 °C
Fe	21.47	21.56	26.28	27.45	1.12	0.75	3.60	2.79
Cr	19.61	19.69	24.36	24.60	0.60	0.38	0.81	0.55
Co	0.31	0.32	0.35	0.36	0.21	0.20	0.17	0.16
Mo	1.76	1.77	2.11	2.07	0.54	0.54	0.20	0.16
Nb	3.24	3.12	0.43	0.17	20.33	20.70	7.54	7.55
Ti	1.18	1.21	0.14	0.04	3.93	3.60	7.60	7.38
Al	1.27	1.19	0.37	0.20	0.20	0.16	8.47	8.85
Mole percent		99.61%	79.90%	76.72%	9.44%	10.90%	10.22%	11.45%
Element	Bulk at.%	MC		$Cr_{23}C_6$				
		1093 °C	718 °C	718 °C	621 °C			
Ni	50.94	–	–	0.51	0.25			
Fe	21.47	–	–	1.81	1.41			
Cr	19.61	0.07	0.02	66.90	67.45			
Co	0.31	–	–	0.01	-			
Mo	1.76	0.16	0.25	10.10	10.19			
Nb	3.24	36.35	50.60	–	–			
Ti	1.18	17.20	3.19	–	–			
Al	1.27	–	–	–	–			
C	0.19	46.22	45.94	20.69	20.69			
Mole percent		0.39%	0.42%	0.005%	0.93%			

The balance is nickel and the results are in atomic percent.

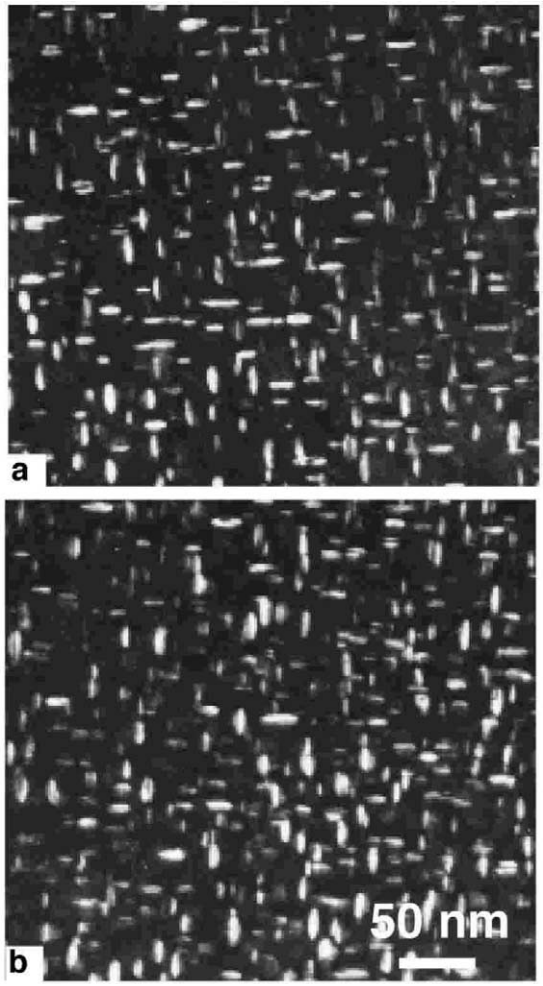

Fig. 1. Dark field transmission electron micrographs taken with a DO_{22} superlattice reflection of the distribution of fine precipitates in Alloy 718: (a) after 8 h at 718 °C and (b) after 8 h at 718 °C, a slow cool at a rate of 55 K h^{-1} to 621 °C, 8 h at 621 °C and an air cool to room temperature.

The microstructure of this Alloy 718 was characterized with a combination of atom probe tomography and analytical electron microscopy. The atom probe tomography characterizations were performed with an energy-compensated optical position-sensitive atom probe (ECOPoSAP) with a specimen temperature of 50–60 K, a pulse fraction of 20% and a pulse repetition rate of 1500 Hz. Transmission electron microscopy was performed with Philips EM400T and CM12 analytical electron microscopes equipped with Link LZ5 EDS/AN10/85S analyzers.

3. Thermodynamic predictions

The equilibrium compositions and amounts of phases present in Alloy 718 at different temperatures were calculated with the use of Thermocalc™ version M and a commercial 12 element Ni–Fe database [2]. The phases considered in the calculation were face centered cubic γ, $L1_2$-ordered γ', DO_{22}-ordered γ'', σ, Laves, MC, M_6C, $M_{23}C_6$, M_7C_3 and liquid. It was necessary to suppress the orthorhombic Ni_3Nb δ phase from the calculations due to the interference with the γ'' phase.

The thermodynamic predictions of the phase compositions and their molar fractions at 718 and 621 °C are shown in Table 1. At 1093 °C, the only phases predicted to be present were the γ matrix and a small volume fraction of NbC carbide. At 718 and 621 °C, γ'', γ' and σ phases were also predicted to be present. A small volume fraction of $Cr_{23}C_6$ was also predicted to be present at 621 °C. These calculations predicted that

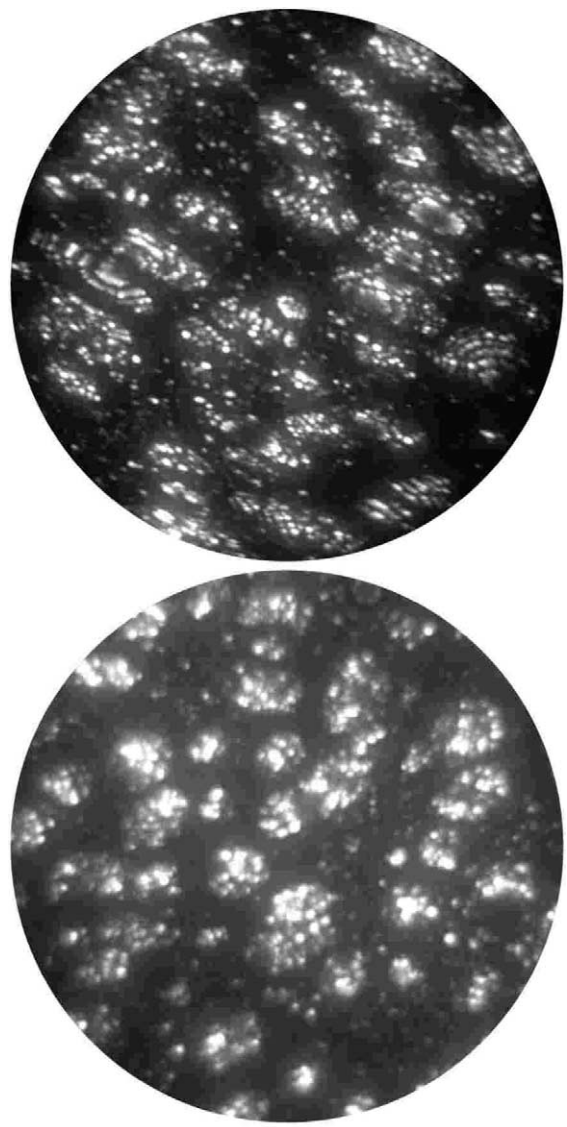

Fig. 2. Field ion micrographs of the distribution of brightly-imaging fine precipitates in Alloy 718: (a) after 8 h at 718 °C and (b) after 8 h at 718 °C, a slow cool at a rate of 55 K h^{-1} to 621 °C, 8 h at 621 °C and an air cool to room temperature.

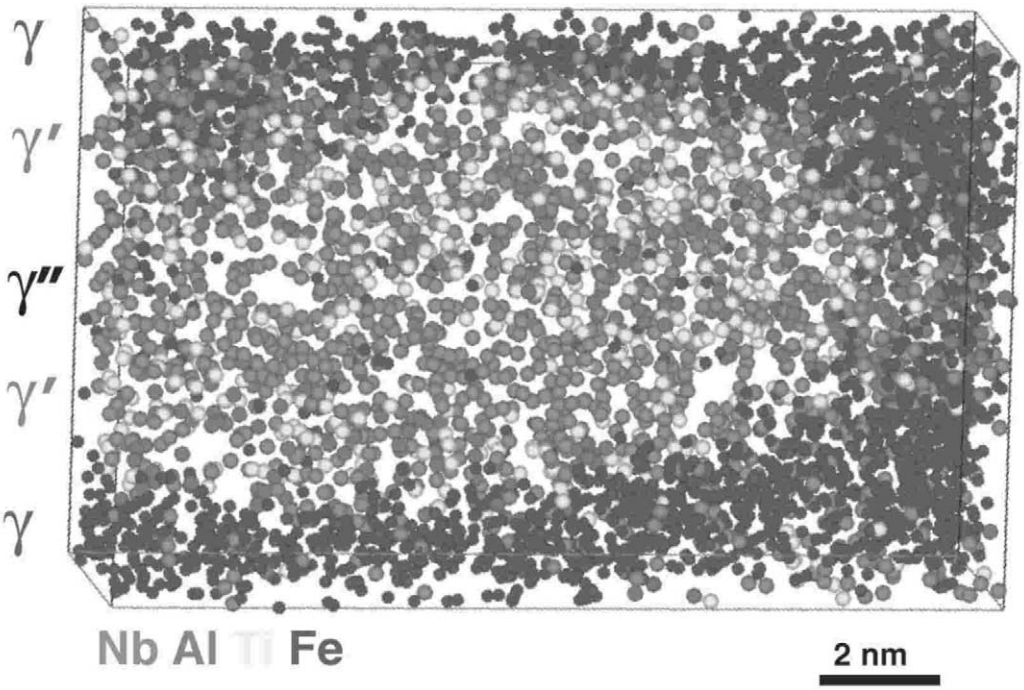

Fig. 3. Atom map of the interior of a fine precipitate. Each sphere represents the position of an individual atom. Only niobium, aluminum, titanium and iron atoms are shown for clarity. The dual phase nature of this precipitate is evident by the two γ′ regions enriched in aluminum and titanium and the central γ″ region enriched in niobium.

iron, chromium, cobalt and molybdenum partition preferentially to the γ matrix, niobium and titanium partition to the γ″ phase and approximately equal levels of aluminum, titanium and niobium partition to the γ′ phase. Niobium, titanium and carbon were predicted to be present in a small volume fraction of NbC carbides at both 1093 and 718 °C and chromium, molybdenum and carbon to be present in $Cr_{23}C_6$ carbides at 621 °C. Chromium, iron, nickel, and molybdenum were also predicted to be present in a small volume fraction of σ phase at both 718 and 621 °C. Compared to those at 718 °C, the predictions at 621 °C showed that the molar fractions of the γ″ and γ′ phases increased and the γ matrix decreased. The iron and chromium levels decreased in the γ″ and γ′ phases and increased in the γ phase. Similarly, the niobium, aluminum and titanium levels decreased in the γ phase, and the niobium level increased and the titanium level decreased in the γ″ phase.

As the σ phase was not observed experimentally, a second set of predictions was also calculated with the σ phase suppressed and the results are given in Table 2. It was also necessary to suppress the Laves phases when the σ phase was suppressed. When the σ and Laves phases were suppressed in the calculations, the molar fraction of the γ matrix increased and the chromium and molybdenum levels in the γ matrix increased. In addition a trace of the $Cr_{23}C_6$ carbide was predicted to form at 718 °C.

4. Microstructure

Transmission electron microscopy of this alloy has revealed a uniform distribution of precipitates in the γ matrix, as shown in Fig. 1. No significant difference in the microstructure was noted between the 8 h at 718 °C and subsequent stages of the heat treatment. The size of these precipitates was approximately 5–13 nm. No other intragranular phases, such as δ and Laves, were observed. All the grain boundaries were free of δ, Laves and NbC precipitates. The low chromium level of this particular Alloy 718 may be significant in suppressing the formation of δ and chromium-enriched Laves phases. However, a few coarse (1–2 μm) MC-type inclusions were observed. No σ phase precipitates were observed. Field ion micrographs of the intragranular precipitates are shown in Fig. 2. As with the transmission electron micrographs, no difference was discernable between the precipitates after the different stages of the heat treatment.

As in previous investigations of Alloy 718, atom probe tomography has revealed that the intragranular precipitates consisted of regions of γ″ and γ′ phases. An example of the dual phase nature of the precipitates is shown in the atom map in Fig. 3. The size of the precipitates was in agreement with the transmission electron microscopy estimates. The compositions of the phases, as determined by selective volume analysis in the 3DAP, are summarized in Table 3. Each composi-

tion listed is the average value of several regions. The partitioning of the alloying elements was found to be in agreement with the thermodynamic predictions in that iron and chromium partition to the γ matrix, niobium and titanium partition to the γ″ phase, and aluminum, titanium and niobium partition to the γ′ phase. In addition there was a general agreement between the measured and predicted compositions. Some minor differences were observed between the atom probe measurements and the equilibrium compositions predicted by thermodynamic calculations. The niobium level in the γ matrix was slightly higher than the predictions. The iron, chromium, molybdenum and titanium levels were slightly higher than predicted in the γ″ phase. The iron level was lower and the molybdenum level was higher than predicted in the γ′ phase. Some of these differences may be due to the compositions of the phases not attaining equilibrium due to the multistep heat treatment and the relatively short times of the heat treatment.

5. Conclusions

The results of this study indicate that caution should be taken in the application of the Ni–Fe database/Thermocalc™ to superalloys because some of the predicted phases may not correspond to actual microstructure of commercial alloys. When microstructural information is taken into account and absent phases are suppressed in the calculations, reasonable agreement between the atom probe data and the thermodynamic predictions may be achieved. These results also indicate that microstructural characterization is an essential component in the alloy design process.

Table 3
Compositions of the phases as determined by atom probe tomography after the 718 °C and 621 °C stages of the heat treatment

Element	γ	
Balance Ni	718 °C	621 °C
Fe	25.54 ± 0.18	26.92 ± 0.17
Cr	23.48 ± 0.17	25.25 ± 0.17
Co	0.38 ± 0.02	0.47 ± 0.02
Mo	2.13 ± 0.05	2.50 ± 0.05
Nb	1.59 ± 0.04	0.99 ± 0.03
Ti	0.47 ± 0.02	0.21 ± 0.01
Al	0.58 ± 0.03	0.34 ± 0.02
	γ″	
Fe	2.11 ± 0.22	1.73 ± 0.20
Cr	2.16 ± 0.22	1.93 ± 0.22
Co	0.05 ± 0.03	0.19 ± 0.07
Mo	1.30 ± 0.17	3.00 ± 0.27
Nb	20.07 ± 0.68	19.27 ± 0.68
Ti	5.59 ± 0.36	4.73 ± 0.34
Al	0.35 ± 0.09	0.44 ± 0.10
	γ′	
Fe	2.00 ± 0.13	2.24 ± 0.23
Cr	0.79 ± 0.08	0.83 ± 0.14
Co	0.09 ± 0.03	0.10 ± 0.05
Mo	0.53 ± 0.07	1.38 ± 0.18
Nb	7.22 ± 0.24	7.54 ± 0.43
Ti	7.38 ± 0.25	8.24 ± 0.44
Al	9.11 ± 0.27	8.79 ± 0.46

The values are quoted in atomic percent and the errors are one standard deviation.

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