A STUDY OF EFFECTS OF PHOSPHORUS, SULFUR, BORON AND CARBON

ON LAVES AND CARBIDE FORMATION IN ALLOY 718

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Abstract

Alloy 718 base chemistries were modified with additions and/or deletions of P, S, B, Si and C to determine the effect of various minor or residual elements on eutectic solidification products in alloy 718-type compositions. The chemistries were such that single additions and interactions could be evaluated. The combinations studied were very clean base alloy, +P, +B, +Si, +BC, +SC, +BSPCSI and commercial 718. Differential thermal analysis (DTA), metallography and energy dispersive x-ray analysis were used to evaluate the solidification path and products. DTA provided significant information on the solidification behavior of these alloys. It was found that B, Si and P were significant Laves formers when present alone. In the presence of C, the solidification moved toward proeutectic carbide formation with the elimination of Laves phase. Sulfur had little effect on the solidification path. It was found that the clean alloy showed little tendency toward Laves formation with the residual elements. This suggests that P, B, and Si determine the Laves forming behavior of Nb. Applications of these results to alloy design, microstructure and solidification cracking are discussed.

Introduction

Studies (1-3) have shown that alloy 718 solidifies in the following sequence: $L \rightarrow L + \gamma \rightarrow L + \gamma + \text{NbC} \rightarrow \gamma + \text{NbC} + \text{Laves}$, where NbC is a secondary solidification product and Laves phase is formed through a terminal solidification reaction. Nb, one of the essential elements in alloy 718, is a primary element associated with Laves phase and carbides. Its role in the formation of Laves is illustrated by Eiselstein's pseudo-binary phase diagram for alloy 718 [Figure 1]. In general, the higher the Nb content, the greater the volume fraction of Laves phase formed in the solidification microstructure, given the same cooling rate.

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Little is published about the effects of minor additions or impurity elements such as carbon, boron, phosphorus and sulfur on carbide and Laves solidification in alloy 718. This knowledge should aid in understanding their effects on solidification, fracture toughness, solution heat treatment, and weld heat affected zone liquation cracking. A recent empirical study strongly correlated boron with the alloy's susceptibility to weld heat affected zone liquation cracking, while the effect of carbon appeared to be neutral [4]. Such empirical studies are of great value to both the industrial and research communities. For the research community, such studies provide both a ready source of research alloys and give direction to the goals of more basic research in the area. The purpose of this research is to define the mechanisms by which minor alloy additions and impurities affect solidification. The role of solidification on weld heat affected zone liquation cracking is discussed and ties are made between composition, solidification and weldability related to liquation cracking. Experimental alloys were obtained from the investigation of the previous study [4] in hope of defining the mechanisms behind their empirical correlations. To this end, a series of experimental alloys, containing C, B, P and S, were used as the test group. Effects of these elements on Laves phase and carbide formation were examined using differential thermal analysis (DTA) and microstructural characterization. A Gleeble, rapid thermal processing machine was also used to assess the relative resistance of the alloys to liquation induced by rapid thermal cycles.

Figure 1 - Alloy 718 pseudo-binary phase diagram.

Figure 3 - The thermal cycle used in the DTA experiments.

Experimental Details

Materials

The chemical compositions of the alloys used in this study are given in Table I. They were designated as 0-718, B-718, S-718, P-718, CB-718 and 718 (commercial). The alloy designated 0-718 was a 718-type alloy with very low concentrations of control elements. The alloys B-718, S-718 and P-718 were doped with boron, sulfur and phosphorus, respectively. CB-718 was doped with both carbon and boron. A commercial 718 alloy was also used as representative of a "traditional" alloy 718 composition.

Table I Chemical Compositions*

Heat	C	Nb	S	P	B	Si	Fe	Mo
8	.1	5.4	0.015	<.001	<.001	<.001	17	2.5
10	.1	4.4	0.015	<.001	<.001	<.001	17	3.5
3	<.001	5.4	0.015	0.015	0.01	<.001	17	3.5
15	<.001	4.4	0.015	0.015	0.01	<.001	22	3.5
S-718	.021	4.4	.004	.001	.002	.01	17	3.2
0-718	<.001	4.4	<.001	<.001	<.001	<.001	22	2.5
B-718	<.001	5.4	<.001	<.001	.01	<.001	17	3.5
P-718	<.001	5.4	.015	.015	<.001	<.001	22	3.5
CB-718	.1	4.4	<.001	<.001	.01	<.001	17	3.5
718	.03	5.0	N/A	N/A	.003	.11	19	2.3

The as-received materials were 7cm x 5cm x 6mm square plates. Since the grain size varied from sample to sample and plate to plate, the as-received materials were cold worked by 30% reduction in thickness and annealed at 950°C to recrystallize the microstructure. The recrystallized materials were homogenized in vacuum-sealed quartz tubings at 1100°C for one hour, followed by a water quench. Subsequent Gleeble and DTA experiments were carried out on the homogenized materials. Microstructures of the homogenized materials are given in Figure 2. As seen from this figure, alloy CB-718 contained a fairly large amount of NbC. Alloy B-718 contained a small amount of Laves particles in the γ matrix. Alloy 0-718 was essentially a single-phase material.

DTA

The DTA experiments were performed using a Perkin-Elmer 1700 cell coupled with a Perkin-Elmer 3600 data acquisition system. The DTA cell was calibrated using pure Ni (>99.999%). The precision of this system, using Pt-Rh thermocouples, was determined to be better than $\pm 5^\circ\text{C}$. Five specimens of each alloy were tested under identical conditions as shown in Table II.

Figure 2 - Microstructures of the alloys after the heat treatment of 1100°C 1 hr + water quench. The heats are: (a) O-718, (b) B-718, (c) P-718, (d) S-718, (e) CB-718, and (f) 718.

Table II Experimental Conditions of DTA

reference material -----	high purity Nickel
crucible material -----	high purity Al_2O_3
scan rate -----	20°C/min
flowing gas -----	high purity He
sample weight -----	≈200 milligrams

The thermal cycle for DTA is shown in Figure 3. For the heating run, the sample was first heated at a fast rate (around 100°C/min) to 900°C and then heated at a rate of 20°C/min from 900°C to 1420°C. For the cooling run, the sample was first held for five minutes at a peak temperature above the liquidus to achieve thermal equilibrium in the cell before it was cooled at a rate of 20°C/min to 900°C. The solidified sample was subsequently cooled at the fastest rate that the system could attain (that is, around 150°C/min). The DTA curves were recorded for the temperature range from 900°C to 1400°C. Reaction temperatures were determined by finding the temperature at which the DTA curve deviated from the local baseline.

Gleeble

An 8mm × 3mm × 1mm specimen was rapidly heated to the peak temperature in 8 sec and then water quenched to room temperature using a Duffers 1000 Gleeble thermomechanical device. Four different peak temperatures were chosen: 1190°C, 1210°C, 1230°C and 1250°C. Chromel-Alumel thermocouples 0.075mm in diameter were welded on the center of the strip specimen to monitor the temperature change. The gauge length of the specimens was 25mm.

The thermally cycled specimens were cut at the midsection of the gauge length in the transverse direction and then mechanically ground and polished to expose the cross section showing the thermocouple junction. Metallography was performed to show the liquation patterns of individual alloys at different peak temperatures.

Metallography

Metallography was performed on the resolidified DTA specimens and the Gleeble specimens. Polished specimens were electro-etched at room temperature for 5 sec in 10% oxalic acid at 5 volts prior to examination using both reflected light and scanning electron microscopy (SEM). Chemical analysis of phases present in the microstructures were performed using the SEM energy dispersive spectroscopy (EDS) technique. The accelerating voltage was 20 KV for EDS analysis. $K\alpha$ x-ray lines were used for the analyses of all elements except for Mo and Nb, where $L\alpha$ lines were used.

Results and Discussion

DTA

The data obtained from the DTA thermograms for these alloys are tabulated in Tables III. As shown by the typical DTA thermograms and the resolidification microstructures in Figure 4, three types of solidification path were observed. The three types differed with respect to the carbide and Laves transformations on cooling. The DTA cooling curve for commercial alloy 718 showed three peaks, indicating, sequentially, the γ matrix solidification, carbide solidification and Laves formation, in the order of descending temperatures [Figure 4a]. All Laves particles were found in the interdendritic regions of the solidification microstructures, indicating that they were products of terminal solidification. Most carbide particles, on the other hand, were observed outside the interdendritic areas, which suggests that carbide was a secondary solidification product.

Table III Summary of DTA Results

Alloy	γ Liquidus	γ solidus	NbC _{start}	NbC _{finish}	Eutectic	ΔT_S^*
Solidification						
CB-718	1332	-	1320	1270	-	62
B-718	1319	-	-	-	1145	174
P-718	1338	-	-	-	1150	188
O-718	1325	1277	-	-	-	48
S-718	1330	-	1235	1191	1110	220
718	1312	-	1243	-	1140	172
Melting						
CB-718	1338	-	1318	1269	-	69
B-718	1321	1225	-	-	-	96
P-718	1328	-	-	-	1180	148
O-718	1338	1271	-	-	-	67
S-718	1345	-	1282	1236	1160	185
718	1331	-	1270	1245	-	86

* ΔT_S - Solidification Temperature Range ($^{\circ}\text{C}$)

* ΔT_M - Melting Temperature Range ($^{\circ}\text{C}$)

DTA - Carbon

With the absence of carbon, it is readily understood that the alloy would solidify without the carbide reaction. This was shown by the DTA cooling curve of the undoped alloy, O-718 [Fig 4b], where the secondary peak associated with carbide formation was absent. The same thing was observed on the cooling curves of other carbon-free alloys [Fig 4c]. Terminal Laves solidification took place in all carbon-free alloys selected for this study as shown by a fairly sharp peak on their DTA cooling curves.

Figure 4 - DTA thermograms for the melting and solidification of various alloys. The heats are: (a) O-718, (b) P-718, (c) S-718, (d) CB-718, (e) B-718, (f) 718, (g) #15, (h) #10.

Figure 4 (continued) - (i) #3, and (j) #8.

Interestingly, when carbon was added in this alloy at 0.1 wt%, as in the alloy CB-718, the entire solidification process was terminated by the carbide reaction and Laves phase was not formed in the solidification microstructure [Fig. 4d]. This was in contrast with the situation of a lower carbon content as in commercial 718, where Laves phase still formed in appreciable quantities. The mechanism may be illustrated in Figure 5 which shows two hypothetical solidification paths that can occur corresponding to high-carbon and low-carbon levels. The path 1-2-3 represents the solidification path of a high-carbon 718-type alloy: $L \rightarrow L + \gamma \rightarrow \gamma + \text{NbC}$. The path a-b-e represents the solidification path of a lower-carbon 718 alloy: $L \rightarrow L + \gamma \rightarrow \gamma + \text{NbC} + L \rightarrow \gamma + \text{NbC} + \text{Laves}$. Thus, a high carbon content in 718-type compositions suppressed the Laves reaction while boron, phosphorus and sulfur all tended to promote the Laves formation. The solidification range in a high-carbon alloy was greatly reduced due to the absence of Laves solidification, as compared to a composition with lower carbon.

Figure 5 - Liquidus projection of the pseudoternary γ -NbC-Laves. Two different solidification paths of alloy 718 due to different carbon levels are indicated: the path 1-2-3 (high-carbon alloy 718) and the path a-b-e (low-carbon alloy 718).

Figure 8 - SEM-EDS spectrum for a liquated particle in B-718 (1190°C/WQ).

DTA - Niobium

It must be noted that the alloy CB-718 containing high carbon content also had a low niobium content which could also contribute to reduced Laves formation. Thus, it was also necessary to evaluate the effect of high and low Nb concentration on Laves formation. This was done by investigating Heats 3, 8, 10 and 15 given in Table I.

Alloys 8 and 10 were of interest to evaluate the ability of the high carbon level to prevent Laves formation when the Nb concentration was also high. Alloys 3 and 15 were of interest to evaluate the tendencies to form Laves when no carbon was present and the Nb level was also low.

Microstructures from these DTA specimens [Fig 6] showed that when carbon was high and Nb was low, neither Laves nor dendritic coring was observed. When both carbon and Nb were high as in alloy 8, it was very difficult to detect any Laves but a small amount may have been present. When both carbon and Nb were low, some Laves was detected and dendritic coring was also present but both were in small volume fractions. When carbon was low and Nb was high, relatively large amounts of Laves and coring was present.

Thus, a 718-type composition with a high carbon and low Nb modification suppressed the Laves reaction. As a result, the solidification range was greatly reduced and the low temperature eutectic was completely eliminated due to the absence of Laves solidification.

Liquation

Liquation encountered in multi-phase alloys subjected to rapid thermal cycles can be classified as two types: (1) constitutional liquation and (2) incipient bulk melting. Pepe and Savage [5] defined constitutional liquation as the equilibrium melting at the interface between the matrix and a second phase particle which fails to completely dissolve in a rapid thermal cycle before the temperature exceeds the eutectic. Thus, a prerequisite for constitutional liquation is the presence of two or more phases in the initial microstructure before a material is subjected to a rapid thermal cycle. Incipient bulk melting, on the other hand, occurs when an alloy is heated above its solidus temperature and some grain boundaries start to liquate as an indication of the onset of bulk melting.

As seen from Figure 7, constitutional liquation of Laves particles was observed in the Gleeble specimen of the alloy B-718 heated to 1190°C and water quenched. (Figure 8 shows a typical SEM-EDS spectrum of this liquated phase, which helped identify this phase as Laves.) When this alloy was heated to

Figure 6 - Microstructures of the solidified DTA specimens of various alloys: (a) O-718, (b) S-718, (c) P-718, (d) B-718, (e) CB-718, (f) 718.

a higher peak temperature such as 1250°C, both constitutional liquation and bulk melting were observed (Figure 9). By comparison, there was no indication of incipient bulk melting in the microstructures of the Gleeble specimens of CB-718 for all chosen peak temperatures. In fact, according to the on-heating DTA results (Table III), the solidus of this alloy was about 1270°C, which was higher than the highest peak temperature (1250°C) used in the Gleeble testing. This is why no grain boundary liquation characteristic of incipient bulk melting was observed for the alloy CB-718 in the present study. However, constitutional liquation of carbides at 1250°C was evidenced by the presence of partially melted NbC particles (Figure 9). This indicates the strong effect that the solidification microstructure had on both the solidification and melting ranges of the alloy. It further suggests that boron has a less well defined effect on the solidification range than did the microstructure.

Figure 7 - Microstructures of the gleeble specimens that have been rapidly heated to 1190°C within 8 seconds and water quenched from the peak temperature. Heats: (a) O-718, (b) P-718, (c) B-718, (d) CB-718.

Figure 9 - Microstructures of the gleeble specimens that have been rapidly heated to 1250°C within 8 seconds and water quenched from the peak temperature.

The microstructures of the rapidly heated Gleeble specimen of the undoped alloy (0-718) did not show any evidence of constitutional liquation. This is understood because the initial microstructure did not contain any second phase such as Laves or NbC. However, when it was rapidly heated to 1250°C and immediately followed by water quench, the grain boundaries in this alloy started to "bow", which may be an indication of incipient bulk melting (Figure 9).

Laves-NbC- γ Pseudo-ternary Model

A basic pseudo-binary phase diagram for alloy 718 was first

drawn by H.L. Eiselstein [1] and it involves two "components": the 718 alloy base and the Nb solute content [Fig 1]. This pseudo-binary phase diagram is of the simple binary eutectic type. It may be taken as a solidification constitution diagram to illustrate the solidification sequence of a carbon-free alloy 718, where the primary γ first crystallizes out of the melt and then the eutectic γ /Laves may form, terminating the solidification process. This solidification sequence is:

The main argument for the application of this simplified pseudo-binary model to the study of commercial alloy 718 is that the γ /Laves is the most predominant microconstituent in the solidified microstructure of commercial alloy 718 [1]. However, this may not be the case with high-carbon doped cast 718 where NbC can form in appreciable quantities and act as a significant "component" of the alloy system. The same is true for 718 alloys following extensive homogenization to remove Laves phase.

Recently, Radhakrishnan and Thompson [6] presented a pseudo-ternary phase diagram consisting of γ , NbC, and Laves phase with a quasi-ternary eutectic composition assumed to be very close to the γ -Laves binary side. In contrast to the binary model (Figure 1), where NbC formation was treated as a separate reaction, this ternary model suggests that NbC should form over a temperature range. Also, this new model holds that there exist a ternary eutectic-type phase relationship among the three major phases, γ , NbC and Laves, that occur sequentially during solidification. The relative amounts of these three phases produced through the ternary eutectic reaction are determined by the lever rule with respect to the eutectic isotherm. Since the quasi-ternary eutectic composition is assumed to be very close to the γ -Laves binary side for this pseudo-ternary system, the amount of the ternary eutectic NbC produced can be highly divorced. The carbide may epitaxially grow on the existing NbC particles that have previously formed through the monovariant reaction $L \rightarrow \gamma + \text{NbC}$.

The above model explains fairly well the observation that a high-carbon and low-Nb 718-type composition solidifies along the path, $L \rightarrow L + \gamma \rightarrow \gamma + \text{NbC}$, where the process is terminated by a carbide reaction, and a lower-carbon or high-Nb alloy 718 solidified with the eutectic-Laves reaction being the final step of solidification. However, both boron and phosphorus tended to promote Laves formation and the mechanism by which this occurred is still not known. It should be noted that the alloys B-718 and P-718 also had the higher Nb content, which could also contribute to increased Laves formation.

Implications for Superalloy Design

Laves phase formed in cast 718 is generally believed to have adverse effects on mechanical properties. It can reduce room

temperature yield strength and ductility [7] and it may adversely affect the subsequent forging due to its low-melting nature [8]. Also, it was observed that the Laves phase was detrimental to the weldability of the alloy [9,10]. Thus, to further improve the performance of alloy 718, the Laves phase can be minimized in the microstructure.

The solidification data obtained by DTA studies, combined with metallographic analysis in this study, suggest that this can be done to some extent by optimizing the concentration of carbon and boron as well as other impurity elements such as phosphorus and possibly sulfur. For example, a carbon level higher than that in the commercial 718 is expected to minimize the Laves formation. However, too high a carbon content can result in a stringer morphology of carbides, which in turn may lead to premature cracking caused by low cycle fatigue under severely stressed conditions as experienced by gas turbine engines.[11]

The present study also suggests that 0.01 wt% B or 0.15 wt% P plus 5.4 wt% Nb in low-carbon alloy 718 tends to enhance the formation of the terminal eutectic Laves in cast 718 and to decrease the solidus of the γ matrix of this alloy. These composition effects are expected to give a lower liquation temperature in the cast alloy 718 when it is rapidly heated as in fusion welding processes. Kelly [4] studied the compositional effects on the weldability of cast 718 using a similar but extended set of modified 718-type alloy samples with various minor additions. He found that boron was the most detrimental element in the sense that it appeared to aggravate the weld heat-affected-zone (HAZ) liquation cracking, while carbon was reported to be neutral to the weldability. This seems to correlate with the results of the present study, in which a high boron content plus a high niobium content was found to enhance the formation of the eutectic Laves and to suppress the solidus of the γ matrix, both of which cause the alloy to liquate at a much lower temperature. Carbon, on the other hand, altered the solidification sequence so as to suppress the formation of Laves and result in a much higher liquation temperature.

It is interesting to note that boron in the high-carbon alloy CB-718 did not have the same effect as found in the carbon-free alloys; it did not directly promote Laves formation or depress the solidus of the matrix if the NbC reaction was the termination of solidification. This suggests that increasing carbon content in alloy 718 will minimize possible detrimental effects of boron on the weldability of this alloy.

All the above implies that high carbon content, reduced impurities, minimum Nb plus intermediate boron content may result in an optimum combination of the following desirable mechanical properties:

1. Good creep properties due to sufficient amount of boron addition [12];

2. Good stress-rupture ductilities due to formation of high volume fraction of carbides [13];
3. Improved room temperature tensile strength and ductility due to elimination of Laves phase [7];
4. Minimized susceptibility to the weld HAZ liquation cracking due to the absence of the low-melting Laves phase and due to the raised grain boundary liquation temperature in high-carbon alloy 718.

Concluding Remarks

This study has shown that a high-carbon low-niobium alloy 718 would solidify without the formation of Laves phase. The addition of boron, phosphorus or sulfur in a lower-carbon alloy 718 tends to promote Laves formation. In view that boron is an essential element in alloy 718 for improved creep properties, it is not advisable to eliminate boron in the alloy base composition. However, high carbon and minimal niobium and impurity contents in this alloy are recommended in order to eliminate the detrimental Laves phase.

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References

1. G. A. Knorovsky, M. J. Cieslack, T. J. Headley, A. D. Romig, Jr. and W. F. Hammeter, "Inconel 718: A Solidification Diagram," Meta. Trans., vol. 20A, Oct (1989), 2149-2158.
2. G. K. Bouse, "Application of a Modified Phase Diagram to the Production of Cast 718 Components," in E.A. Loria (ed), Superalloy 718: Metallurgy and Applications, TMS (1989), 69-77.
3. B. Radhakrishnan and R. G. Thompson, "Phase Diagram Approach to Study Liquation Cracking in Alloy 718," accepted for publication in Met. Trans. (1990).
4. T. J. Kelly, "Elemental Effects on the Cast 718 Weldability," Welding Journal, vol. 68, (1989), 44-51.
5. J. J. Pepe and W. F. Savage, Weld J., 46, 411s (1967).
6. B. Radhakrishnan and R. G. Thompson, "Solidification of the Nickel-Base Superalloy 718: A Phase Diagram Approach," Met. Trans., vol. 20A, Dec (1989), 2866-2868.
7. R. M. Evans, "The Welding and Brazing of Alloy 718," DMIC Report 204, Battelle Memorial Institute, June (1964).

8. G. C. Gould, "Freckle Segregation in Vacuum Consumable Electrodes Ingots," Trans. TMS-AIME, vol. 233, (1965), 1345.
9. E. G. Thompson, "Hot Cracking Studies of Alloy 718 Weld Heat-Affected-Zone," Welding Journal, vol. 48, No. 2, (1969), 70s-79s.
10. W. A. Baeslack, III and D. E. Nelson, "Morphology of Weld Heat-Affected-Zone Liquation in Cast Alloy 718," Metallography, vol. 19, (1960), 371-379.
11. J. M. Moyer, "Extra Low Carbon Alloy 718," in ref. 34, 445-456.
12. R. F. Decker and J. W. Freeman, "The Mechanism of Beneficial Effects of Boron and Zirconium on Creep Properties of a Complex Heat resistant Alloy," Trans. AIME, vol. 218, (1960), 277.
13. J. P. Stroup and L. A. Pugliese, "How Low-Carbon contents Affect Superalloys," Metal Progress, vol. 99, No. 2, (1968), 96-100.