PHOSPHORUS - BORON INTERACTION IN NICKEL-BASE SUPERALLOYS

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Abstract

The effect of B on the properties of superalloys has been known for many years and is well documented in the literature. There is, however, very little published information on the effect of P content in Ni-base superalloys. This paper describes the results of an experimental program to study the effects of P content in Allvac 718 and Waspaloy, particularly as it interacts with B content.

Based on a series of sub-scale heats, a strong interaction between P & B on the rupture life of both alloys was discovered. This interaction has not been previously reported. Results showed that B alone had only a very small positive effect on stress rupture life of 718. However, P, which is generally considered to be a harmful impurity element, had a strong positive effect. Most interesting was the observation of a strong interaction between P & B. This effect was synergistic in that the combined effect was much greater than the sum of the individual elements acting independently. More than one order of magnitude increase in stress rupture life was observed over the entire range of B & P contents investigated. A 300-400% improvement in rupture life over typical commercial compositions was obtained with optimum P & B levels.

Dramatically different effects of P & B were observed in Waspaloy. When acting alone, P had only a small positive effect while B strongly improved rupture life. However, when both elements were present, increased P levels drastically deteriorated the beneficial effect of B. Conversely, when P was controlled to ultra-low levels, the beneficial effects of B extend to much higher levels than normal, and improvements in stress rupture life of 300-400% were possible.

The mechanisms of the observed P-B interaction in superalloys are discussed on the basis of the known behavior of P & B, alloy chemistry, and the observed fracture behavior.

Introduction

Minor elements have a profound effect on the performance of nickel-base superalloys and have been extensively studied in the last few decades. Several review papers [1-3] have summarized the major results up to 1984. Minor elements are generally divided into three categories: detrimental, beneficial and neutral elements. The detrimental elements such as S, Se, Te, As, Sb, Bi, Pb and Ag have been thoroughly studied and are tightly controlled in Ni-base superalloys. A large amount of research has also been conducted on the beneficial elements such as B, Mg, Hf, Zr

and rare earth metals. Boron, in particular, has been regarded as a universal strengthening element and is added to almost all Ni-base superalloys to improve creep or stress rupture properties. Most investigators have attributed the beneficial effect of B to increased grain boundary cohesion due to grain boundary segregation of B [4-6], depletion or reduced agglomeration of precipitates in grain boundaries [7], reduced grain boundary concentration of detrimental elements, such as S, through site competition [6,8], and improved slip and dislocation transfer at grain boundaries to prevent the initiation of cracks [9,10].

One element, P, has not been studied in detail. There is also some controversy in the literature concerning the role of P in Ni-base superalloys. Most investigators regard P as a detrimental element which causes grain boundary embrittlement at high temperatures [11], reduces hot workability [12], and damages the resistance to high temperature corrosion [13]. However, early work by Bieber and Decker [14] suggested P, in small amounts, to be beneficial to malleability. Was and his co-workers [15,16] revealed that the addition of P in Ni-Cr-Fe alloy 600 improved the intergranular cracking resistance and creep resistance in Ar or high temperature water. Recent work [17] has demonstrated that increasing the P level of commercial 718 up to 0.022%, which is higher than the maximum level allowable in most specifications, significantly improved stress rupture properties. The increase in stress rupture life or reduction in average creep rate was more than one order of magnitude when P content was increased from a few parts per million to 0.022%. Previous investigators suggest the mechanism of the beneficial effect of P is increased grain boundary cohesion and reduced grain boundary concentration of detrimental elements by site competition [16,18].

It is well known that interaction may exist between minor elements, and this interaction may exert a tremendous effect on the properties of Ni-base superalloys. A typical example is the interaction between S and other beneficial elements such as Mg and rare earth metals. However, very little work has been performed on the possible interaction between the important minor element B and other elements. This work has shown that there is a strong interaction between P and B which can significantly influence the properties of Ni-base superalloys.

Experimental Procedure

Test Materials

A large number of experimental heats were produced covering a wide range of P and B levels. Phosphorus in 718 ranged from < 0.001 % to 0.035% (levels of all elements are in weight percentage) and B from < 0.001 % to 0.020%. Two C levels, < 0.01% and 0.03%, were used. The nominal aim composition of all other elements remained fixed at 18% Cr - 19.2% Fe - 2.9% Mo - 5.25% Nb - 0.95% Ti - 0.6% Al - Bal. Ni. Waspaloy P and B levels ranged from < 0.001 % to 0.022% and < 0.001% to 0.025%, respectively. The test alloys also had two C levels, < 0.01% and 0.035%, and a fixed nominal composition of 19.7% Cr - 13.4% Co - 4.25% Mo - 3.0% Ti - 1.3% Al - Bal. Ni. The 718 alloy with 0.006% P, 0.004% B, 0.03% C and Waspaloy with 0.005% P, 0.005% B and 0.035% C are considered to be typical "commercial" compositions and are the baseline for many of the comparisons made in this paper. Two to three heats were made for some critical chemistries to check the repeatability of test results, but no tabulation of all of the chemistries produced in this study is presented due to the large amount of data.

All test alloys were vacuum induction melted (VIM) with a weight of 23 Kg per heat and cast as 70 mm diameter electrodes. VIM electrodes were further refined by vacuum arc remelting (VAR) to 100 mm diameter ingots. VIM/VAR ingots were homogenized for 16 hours at 1190°C and rolled to 15 mm diameter bars within the temperature range of 1040°C to 920°C for 718 and 1060°C to 960°C for Waspaloy.

Heat Treatment

Specimen blanks for tensile and stress rupture tests were cut from 15 mm rolled bars and subjected to standard heat treatment as follows:

718 was solutioned for 1 hr at 954°C, air cooled and then aged for 8 hrs at 718°C, furnace cooled to 621°C, held at 621°C for 8 hrs, air cooled.

Waspaloy was solutioned for 4 hrs at 1010°C, water quenched and then aged for 4 hrs at 843°C, air cooled, aged for 16 hrs at 760°C, air cooled.

Mechanical Tests

Stress rupture tests of 718 were performed in air at 649°C at applied stress levels of either 669 MPa or 773 MPa. Waspaloy was tested at four different test temperatures / stress combinations: 649°C / 669 MPa, 732°C / 516 MPa, 760°C / 440 MPa and 816°C / 329 MPa. All tests were conducted according to ASTM E292. Two to three specimens were tested at each test condition.

Microstructure and Fractography

Microstructural observation. Microstructures were examined by optical and Scanning Electron Microscope (SEM) before and after stress rupture tests. Special attention was paid to grain structure and phase morphology. A meaningful comparison of microstructural changes between different alloys could not be obtained from broken stress rupture test specimens due to different exposure times and total deformations. A special experiment was therefore performed to generate specimens with equal temperature / stress / time history. Two compositions of both 718 and Waspaloy were selected; one was the nominal commercial composition, and the other alloy had the optimum P and B levels. Stress rupture test specimens from these two alloy pairs were tested at the same conditions: 718 at 649°C / 773 MPa for 36 hrs, and Waspaloy at 732°C / 516 MPa for 13 hrs. The specimens were unloaded after reaching specified test times, and micros were made from the gauge sections.

Fractography. The fracture surface of representative stress rupture test specimens was examined by SEM, and the fracture mode was identified to provide information on the effect of P and B on the fracture process of both alloys.

Experimental Results

Stress Rupture Properties

P and B Effects in Commercial Alloys. Figures 1 and 2 show the effect of changing P on stress rupture life of 718 and Waspaloy with nominally "commercial" levels of B (0.004% and 0.005%, respectively). It can be seen that increasing P had different effects in these two alloys. Rupture life of 718 significantly increased with increasing P level. An order of magnitude increase in life was achieved when P was raised from a few parts per million to 0.022%. However, in Waspaloy rupture life was unchanged or decreased with increasing P, depending upon test temperature. Figures 3 and 4 show the effects on stress rupture life of changing B at a constant, "commercial" level of P (0.006% and 0.005%, respectively). Different behavior was again revealed in these two alloys. Boron showed a significant, beneficial effect on stress rupture life of 718 up to the highest level tested (0.011%), but the beneficial effect of B saturated at about 0.005% in Waspaloy and further additions resulted in only moderate improvements

P and B Effects in High Purity Alloys. To prevent any possible interaction and to isolate the independent effects of P & B, a series of "high purity" heats were produced which varied P at the lowest possible levels of B, and C and B at the lowest levels of P and C. Results are summarized in Figures 5 through 8. Compared to Figures 1 through 4, there are differences in terms of P or B effect:

1. In high purity 718 (< 0.001% B), P also dramatically improved stress rupture life, but there appeared to be a critical P level (0.0075%) below which no significant benefit was observed (Fig. 5, 6). P produced an

Figure 1. Stress rupture life of 718 as a function of P content.

Figure 3. Stress rupture life of 718 as a function of B content.

Figure 2. Stress rupture life of Waspaloy as a function of P content.

Figure 4. Stress rupture life of Waspaloy as a function of B content.

Figure 5. Effect of P level on stress rupture of Alloy 718 with very low levels of C and B.

Figure 7. Effect of B level on stress rupture life of Alloy 718 with very low C and P levels.

Figure 6. Effect of P level on stress rupture life of Waspaloy with very low C and B levels.

Figure 8. Effect of B level on stress rupture life of Waspaloy with very low P and C levels.

insignificant to weakly positive effect in high purity Waspaloy ($< 0.001\%$ B), depending upon temperature (Fig. 6). This contrasts to an insignificant to slightly detrimental effect in commercial Waspaloy (0.005% B, Fig. 2).

2. In the absence of P, B produced a relatively weak improvement in rupture life of 718 (Fig. 7). In Waspaloy, however, the absence of P dramatically accentuates the strengthening effect of B (Fig. 8).

These results show that P as well as B can be beneficial for stress rupture properties of high purity 718 and Waspaloy, but their effects in these two alloys are different. P is a strongly beneficial element in 718 and a weakly beneficial element in Waspaloy, while the reverse is true for B. Further, these results clearly suggest that there is an interaction between P and B and their effects on rupture life of both alloys.

Interaction. The combined or interactive effects of P and B on the rupture life of 718 and Waspaloy are shown in Figures 9 - 12. Figures 9 and 10 illustrate the strong synergistic effect of P and B in 718. If the P content was extremely low, rupture properties were rather poor, and B was almost ineffective as a strengthener. As the P content increased, B became a very potent strengthener. Optimum rupture life was achieved at P and B levels considerably above levels typical of today's commercial practice (0.022% P, 0.011% B vs 0.006% P, 0.004% B).

Strong synergistic effects of P and B were also displayed in Waspaloy (Fig. 11 and 12) although the effects were opposite with regard to P. At very low levels of P ($< 0.001\%$ P), significantly below levels of current commercial practice (nominally 0.005% P), B was an extremely effective strengthening element. With relatively small increases in P content, the strengthening effect of B rapidly diminished, and at typical commercial P levels, boron's effect appeared to saturate at about 0.005% B, i.e. typical commercial B levels. Optimum rupture properties for Waspaloy were achieved with $< 0.001\%$ P, 0.015% B vs typical commercial levels of 0.005% P, 0.005% B.

The variation in rupture properties for both 718 and Waspaloy over the entire P and B composition ranges investigated was greater than an order of magnitude while improvements over typical commercial compositions was more than 300%. Other properties were either unchanged (e.g. room and elevated temperature tensile) or slightly improved (e.g. stress rupture ductility) but are omitted here due to space limitations.

Fractography and Microstructure. For the most part, the stress rupture failure mode for 718 was transgranular, ductile dimple type. Waspaloy consistently failed in an intergranular mode over the entire range of P and B studied (Fig. 13). No significant differences in structure were apparent by either optical or SEM microscopy of alloys with different P

and B levels. The size and quantity of delta phase in 718 and grain boundary carbides in Waspaloy did not vary with composition. Grain size of all samples was consistently fine: ASTM 12 for 718 and 10 for Waspaloy.

Interrupted Stress Rupture Tests. The significant difference in stress rupture properties for both 718 and Waspaloy with different P and B levels was also evident in the interrupted stress rupture tests in Table 1. Alloys with optimum levels of P and B were unbroken and had barely elongated under the same conditions which caused failure and high elongations in alloys of nominal commercial compositions. Metallography of these specimens showed extensive intergranular cracking over the entire gauge length in commercial Waspaloy (G947-1) as opposed to none at all in the optimum alloy (Fig. 14). No intergranular cracks were noted in either 718 sample.

Microhardness tests taken before and after the interrupted stress rupture tests are also shown in Table 1. Results from the undeformed shoulder regions show significant overaging at the test temperature for the normal commercial 718 (G457-1) but very little for the optimum composition (G727-2). Very little change and no difference between the different heats of Waspaloy was apparent.

Discussion

In superalloys, P has generally been treated as a harmful or, at best, a somewhat innocuous trace element, and most specifications limit it to relatively low maximum values (e.g. 0.015% max). This work has shown that this long standing belief is not necessarily true and that the effect of P is, in fact, strongly alloy dependent. It has further been discovered that there is a strong interaction between P and B and that the long recognized stress rupture strengthening effect of B can be very substantially enhanced by controlling P content.

In the absence of B, P has been shown to promote a moderate or weak rupture life improvement in 718 and Waspaloy. When combined with B, however, the results in these two alloys are distinctly different. Maximum rupture life in 718 was obtained at P levels well above those of typical commercial practice while in Waspaloy, optimum results were obtained with P content significantly lower than normal. Optimizing the P content of superalloys also extends the stress rupture strengthening effect of B. At typical commercial P levels, the effect of B appears to saturate at relatively low levels, and adding additional B produces little or no further gain in rupture life. At optimum P contents, however, peak rupture lives were obtained with B approximately three times normal commercial levels and more than double typical specification maximums.

The exact reasons for the above phenomena are uncertain at this time, but it is possible to postulate certain mechanisms which are consistent with what is already known about P and B and the data obtained in this work. Numerous studies have shown that both P (19-22) and B (17, 19, 22, 23) strongly segregate to grain boundaries and compete for

Figure 9. Interaction of P and B with stress rupture life of 718.

Figure 11. Interaction of P and B content with stress rupture life of Waspaloy.

Figure 10. Interaction of P and B with stress rupture life of 718.

Figure 12. Interaction of P and B content with stress rupture life of Waspaloy.

(a)

(a)

(b)

(b)

Fig. 13. Typical stress rupture failure mode in (a) Alloy 718, (b) Waspaloy

Figure 14. SEM photographs of gauge section of Waspaloy interrupted stress rupture samples: (a) Heat G947-1, < 0.001% P, 0.012% B, no intergranular fracture and (b) Heat G753-1, 0.006% P, 0.005% B, extensive intergranular fracture.

Table 1. Results of Interrupted Stress Rupture Tests

Alloy	Heat No.	Chemistry (wt%)			Stress Rupture Test				Shoulder Hardness (HV)	
		C	P	B	T °C	S MPa	t Hr	EL %	Before	After
718	G457-1	0.031	0.006	0.004	649	773	31.9*	24.0	478	455
	G727-2	0.033	0.022	0.011	649	773	36.0	1.2	476	472
WASPALLOY	G753-1	0.035	0.006	0.005	732	516	13.3*	40.1	425	418
	G947-1	0.035	<0.001	0.012	732	516	13.3	2.2	422	419

* Specimens broke at indicated time.

grain boundary sites with P having the stronger tendency to occupy these sites (24,25). Both elements are believed to increase grain boundary cohesion and improve the resistance to high temperature intergranular fracture, but B appears to be much more effective in this regard. Both elements could also segregate to precipitate/matrix interfaces or vacancies to increase the stability of precipitate particles by reducing diffusion rates or interact with dislocations to retard dislocation movement.

In 718, the transgranular failure mechanism and the reduced rate of overaging, shown in Table 1, suggest transgranular dislocation creep as the controlling mechanism and would suggest increased stability of precipitate particles (probably γ'') as the probable cause in the absence of further information as to the location of P and B in the alloy. For Waspaloy, very little change in hardness after interrupted stress rupture testing was shown (although the test time was very short), but a very obvious reduction in the degree of intergranular fracture was observed. This, coupled with the completely intergranular stress rupture fracture mode for Waspaloy, would suggest grain boundary strengthening as the controlling mechanism. It could be postulated that, due to site competition, when P is low, more B can segregate to the grain boundaries, thus improving rupture life. A CRADA program is currently underway with Oak Ridge National Laboratories to better define the mechanisms of stress rupture life improvements which have been observed in this study. With such an understanding, it should be possible to improve the rupture life of a number of existing superalloys and to develop entirely new alloys with superior properties.

Conclusions

The following conclusions have been drawn from this study:

1. This work has demonstrated that P content can play a key role in the stress rupture life of superalloys. Contrary to generally held beliefs, the effect may be positive in some alloys, suggesting a purposeful addition rather than the low maximum limit normally imposed.
2. A strong synergistic interaction between P and B was found. This interaction was alloy specific, but for both 718 and Waspaloy, rupture properties at optimum P and B contents exceeded the results of each element acting independently.
3. At optimum P contents, the usual effect of B on improving rupture life can be extended to B concentrations nearly three times normal.
4. In both alloys, more than an order of magnitude improvement in rupture life was observed over the entire compositional range investigated. Greater than 300% life improvements were measured for optimum P and B compositions compared to nominal commercial compositions.
5. The mechanisms for property improvements noted are still being studied, but data suggest they are alloy specific and may involve competitive grain boundary segregation, interaction of P and B atoms with precipitates, vacancies, or dislocations.

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