STRENGTHENING OF COBALT-BASE ALLOYS BY SECONDARY PRECIPITATION OF CARBIDES

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ABSTRACT

Secondary hardening by carbides has been studied in two cobalt-base superalloy matrices suitable for the manufacture of sheet products: Co-20Cr-10Ni-15W and Co-20Cr-25Ni-10Mo, with 0.1 to 0.2 % C.

It has been shown that a simple solution and ageing treatment suffices to produce considerable carbide precipitation in the molybdenum-containing base, whereas the response of the tungsten reinforced matrix is limited. A small boron addition to the latter enables a copious precipitation of M23C6 carbides to be obtained by a quench and ageing treatment, but the mechanism seems to involve retained vacancies, being inoperative near surfaces and therefore in thin products.

Small additions of MC carbide-forming elements, niobium or titanium, enable a more stable, albeit less abundant, precipitation to be obtained in both bases. With the one exception mentioned above, nucleation takes place on dislocations. While the addition of boron does not greatly modify the carbide distribution in this case, it does have a pronounced effect on creep strength, the mechanism remaining uncertain.

The most promising of the compositions studied, which offers an increase in temperature capability of ~ 80 °C (~ 140 °F) over the existing commercial alloy L 605, has been developed on an industrial scale and has successfully undergone test-bed trials in the form of a primary nozzle convergent component for the Olympus 593 Concorde engine.

Introduction

Work in the author's laboratory and elsewhere (1, 2) on the development of cobalt-base superalloys for sheet manufacture has shown that strengthening by precipitation of intermetallic phases, via Ti and Al additions, is only effective up to about 850 °C. This is due to the rapid increase in solubility of the δ' hardening precipitate as the temperature rises and to the formation of more massive phases, such as Co₃Ti or LAVES phase at higher hardener contents. Furthermore, the relatively rapid γ' precipitation kinetics are not conducive to good weldability. It was therefore decided to examine the possibility of strengthening cobalt-base matrices by enhancing secondary carbide precipitation.

The work was guided by the results of a previous investigation on carbide precipitation in an Fe-Ni-Cr austenitic matrix (3). In this study it was shown that the volume fraction of secondary carbide could be greatly increased by aging after solution at a high temperature followed by rapid cooling, and that this effect was markedly accentuated by small additions of boron. The larger specific volumes of M23C6 and MC carbides compared with that of the f.c.c. matrix (respectively ~ 10 to 15 % and > 100 % greater) render their homogeneous precipitation difficult, necessitating a considerable flux of vacancies towards an embryo in order to enable it to grow. In addition to an increase in supersaturation, solution treatment at higher temperatures, if followed by rapid cooling, enables larger vacancy concentrations to be retained. The influence of boron on carbide precipitation is probably linked to its effect on vacancy retention. The higher thermodynamic stability of MC carbides makes them potentially more efficient for imparting creep strength at elevated temperatures than the more soluble M23C6. It was therefore decided to study the effects of B, Ti and Nb additions on the secondary carbide precipitation in two matrices; Co-20Cr-10Ni-15W and Co-20Cr-25Ni-10Mo, the first of these corresponding to the commercial alloy L 605 or HS 25.

Materials

The chemical compositions of the materials studied are given in table I. The alloys were melted and cast under vacuum, either into 10 kg cylindrical ingots, of mean diameter 90 mm, into sticks of mean diameter 30 mm, or, in one case, into a slab ingot of approximately 40 x 210 mm section. The round ingots were hot-worked by hammer-forging down to 15 x 70 mm bar, while the sticks were first hot-forged to 15 mm diameter bar which was then hot-swaged to a diameter of 12 mm. The 12 kg slab ingot was hot -forged, hot-rolled and finally cold-rolled to 1.6 mm thick sheet.

Results

Aging response

Figure 1 shows the hardening obtained by aging for 16 hours at temperatures between 600 and 1 150 °C, following solution treatment at 1 200 °C, for the W-containing matrix with and without additions of 0.01 % B, 1 % Ti or 1 % Nb. The effect of the rate of cooling from the solution temperature is also indicated. Whereas the plain matrix shows only a slight response to aging and little effect of cooling rate, the presence of boron leads to a marked increase in hardening with a pronounced sensitivity to cooling rate. In all the remaining alloys the carbon content was raised to 0.2 % (or 0.25 % for those with 2 % Ti) in order to increase the carbide supersaturation. In the case of the alloys with W and Ti or Nb additions, a considerable rise in the unaged hardness is observed, with a further increase after aging between 700 and 1 050 °C, the peak being at around 850 °C The effect of cooling rate, studied only for the Ti containing alloys, is small, as is that of boron, which here tends rather to lower the hardness, although the increment in hardening at the peak is slightly greater. No confers a greater hardness than Ti at all temperatures, but the major hardening contribution is already observed in the solution-treated condition. Higher solution temperatures lower the as-solution-treated hardness, but increase the maximum value on ageing. This is shown in figure 2 for the W-containing alloy with 1 % Ti and B, in comparison with the straight matrix, for which there is no significant effect below 1 300 °C.

Table I - Chemical analyses of experimental alloys (wt. %)

Alloy Nº	Ingot type	С	Si	Mn	Ni	Cr	Со	W	Мо	Ti	Nb	В	Fe
Wia	round	0.08	0.19	1.70	10.2	19.9	bal.	14.6	_	_			1.26
W 1 b	round	0.10	0.19	1.64	10.1	19.8	bal.	14.8	-	-	-	-	1.06
W 1 c	stick	0.12	0.03	1.47	10.0	19.9	bal.	14.8	-	-	-	-	N.A.
W 1 d			0.07		1			1	-	-	-	-	N.A.
W 2 a	round	0.09	0.12	1.48	10.0	19.9	bal.	14.9	-	-	-	0.01 *	1.06
W 2 b	round	0.08	0.13	1.51	10.0	19.9	bal.	14.8	-	-	-	0.01	1.02
W 3	stick	0.18	0.07	1.46	10.0	19.9	bal.	15.1	-	0.98	-	-	N.A.
W4a	round	0.19	0.12	1.64	10.1	19.6	bal.	15.3	_	0.97		0.01 *	1.06
W4b	slab	0.19	0.20	1.50	10.0	20.1	bal.	15.2	_	0.98	-	0.01 *	0.10
W4c	stick	0.18	0.08	1.46	10.0	19.8	bal.	15.2	-	1.00	-	0.005	N.A.
W 5	round	0.25	0.19	1.50	10.0	20.2	bal.	15.1	-	1.98	-	0.01 *	0.10
W 6	stick	0.18	0.11	1.45	10.0	20.0	bal.	14.8	_	-	0.95	-	N.A.
W 7	stick	0.18	0.09	1.46	10.0	19.9	bal.	14.4	-	-	1.03	0.008	N.A.
M 1	round	0.20	0.08	1.52	24.4	19.9	bal.	-	10.1	-	- (-	N.A.
M 2	round	0.19	0.03	1.56	25.0	20.1	bal.	-	10.1	-	-	0.005*	N.A.
м 3	stick	0.19	0.13	1.45	25.2	20.0	bal.	-		1.00		-	0.18
M4a	round	0.19	0.12	1.54	25.1	20.2	bal.		9.8	1.02	-	0.005*	N.A.
M4b	1		0.12					-		1.00	-	0.008	0.2
M 5	i		0.12					-	9.8	1.96	-	0.005*	N.A.
M 6	stick	0.17	0.19	1.46	25.2	19.9	bal.	-	10.0	-	1.15	-	0.17
м 7	stick	0.17	0.18	1.46	25.2	19.8	bal.	-	10.0	-	1.08	0.006	0.21

* Target value

N.A. = not analysed

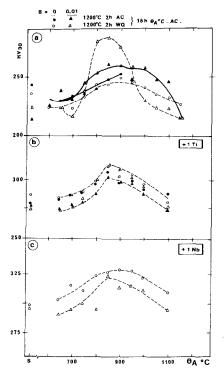


Figure 1 - Aging response of W containing matrix with various additions: alloys (a) W 1 a, W 1 b, W 2 a, W 2 b; (b) W 3, W 4 c, (c) W 6, W 7

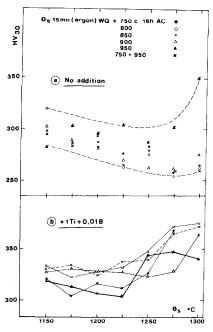


Figure 2 - Effect of solution temperature on aging response: alloys (a) W 1 d; (b) W 4 b. Strip specimens cold rolled 27 % to 1.6 mm before solution treatment

The aging response of the Mo-containing matrix with various additions is illustrated in figure 3. In this case the hardness in the solution-treated condition is only slightly affected by 1 % additions of either Ti or Nb, while B has very little influence. The most pronounced hardening is obtained in the alloys without Ti or Nb.

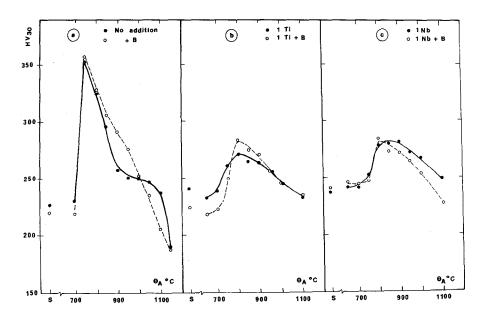


Figure 3 - Aging response of the Mo-containing matrix with various additions. Heat treatment 2 h 1 200 °C WQ + 16 h $\Theta_{\rm A}$ °C. Alloys (a) M 1, M 2, (b) M 3, M 4 b (c) M 6, M 7

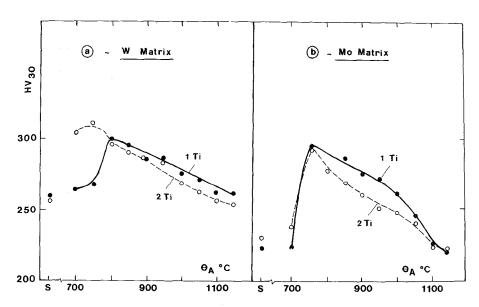


Figure 4 - Effect of Ti content on aging response. Heat treatment 2 h 1 200 °C WQ + 16 h θ_A °C AC. Alloys (a) W 4 a, W 5 (b) M 4 a, M 5

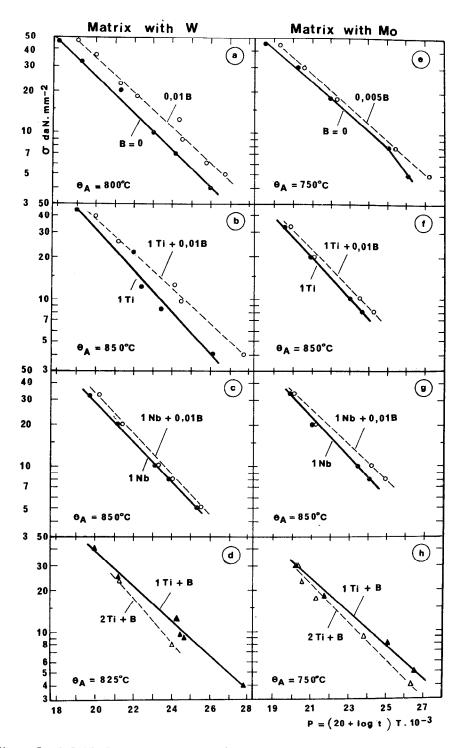


Figure 5 - LARSON-MILLER plots for 0.2 % creep elongation. Heat treatment 2 h 1 200 °C WQ + 16 h Θ_A AC. Alloys (a) W 1 b, W 2 a (b) W 3, W 4 c (c) W 6, W 7 (d) W 4 c, W 5 (e) M 1, M 2 (f) M 3, M 4 b (g) M 6, M 7 (h) M 4 a, M 5

Increasing the Ti content from 1 to 2 % does not lead to significant additional hardening, either in the Mo - or in the W-containing matrices, while in the latter the peak is shifted to a somewhat lower temperature, figure 4.

Creep

The times for 0.2 % creep elongation for alloys solution-treated 2 h 1 200 °C WQ and aged 16 hours at the corresponding peak hardening temperature are plotted in figure 5 in the form of LARSON-MILLER curves. The differences in the creep rupture curves are qualitatively similar, albeit smaller in magnitude, than those for 0.2 % elongation. It can be seen that boron systematically increases the creep strength, the effect being particularly marked for the W-containing matrix with no other addition. In this case, air-cooling the alloy with boron instead of water-quenching after solution treatment led to results intermediate between the two curves shown in figure 5 (a). For both the W-and Mo-containing matrices, increasing the Ti addition from 1 to 2 % leads to a drop in creep strength, particularly at high temperatures. The highest creep strengths were obtained for the the W-containing matrix with 1 % Ti and B, for the Mo-containing matrix with 1 % Nb and B, and for both matrices with simple B additions. However, it will be seen in the following section that the Bassisted hardening in the plain W-containing matrix is absent in the surface regions, making it inapplicable for thin sections (the creep tests were carried out on cylindrical specimens in which the gauge-length was machined sufficiently after aging to remove the surface-affected zone).

The gain in creep strength compared with the alloy L 605 is illustrated in figure 6 for the composition with W, 1 % Ti and B, for three solution treatment temperatures. The increase is especially marked at higher test temperatures where it can amount to 150 °C or over 100 % in stress for the same time to 0.2 % elongation, 80 °C for 1 % elongation and 50 °C for rupture.

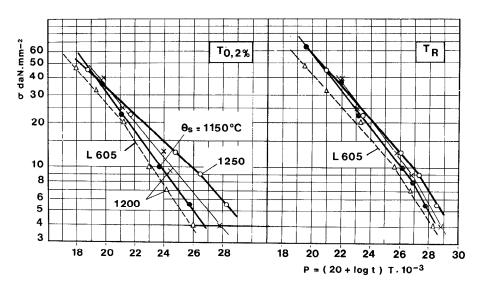


Figure 6 - Effect of solution-treatment temperature on creep strength for W-containing alloy with 1 % Ti and B. Alloys W 1 b, W 4 a. Heat treatment 2 h Θ_8 °C WQ + 16 h 850 °C AC

Microstructure

Microstructures were studied by optical microscopy, replica and thin-foil electron microscopy and by X-ray diffraction, after solution treating and aging to maximum hardness. Figure 7 shows the structure observed in the plain W-containing matrix.

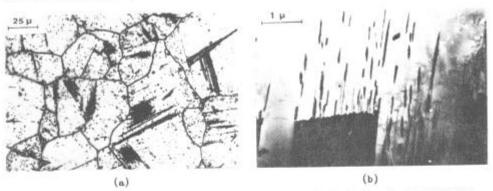


Figure 7 - Plain W-containing matrix. Alloy W 1 c, heat treatment 2 h 1 200 °C WQ + 16 h 850 °C AC, (a) optical micrograph - (b) thin foil

Apart from primary M₆C carbides, intragranular precipitation after aging is sparse, being chiefly limited to film-like M₂₃C₆ on stacking faults, often associated with incoherent twin boundaries. Some M₇C₃ is also occasionally found, while the grain boundaries contain mainly M₂₃C₆ with small amounts of M₆C and LAVES phase. The addition of B brings about a radical change, figure 8. An intense precipitation of fine M₂₃C₆ carbides is obtained, with denuded zones near grain boundaries. Many small dislocation loops are observed with clear evidence that precipitation takes place at least partly upon them. This behaviour is similar to that previously observed in Fe-Ni-Cr alloys (3). Denuded zones are also present at the specimen surface where their depth attains about 2 mm.

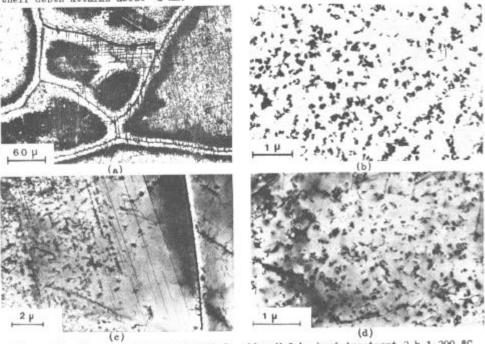


Figure 8 - W-containing matrix with B, alloy W 2 b, heat treatment 2 h 1 200 °C WQ + 16 h 800 °C AC; (a) optical micrograph - (b) replica - (c) and (d) thin foil

In the Mo-containing matrix, on the other hand, B has little effect on the heavy precipitation of M23C6 on dislocations, figure 9, and no surface effect is observed. The microstructures obtained with additions of Ti or Nb are illustrated in figure 10. Here again boron does not seem to affect the microstructure. In the matrix with W and 1 % Ti, TiC is observed in the form of primary carbides and as thin platelets precipitated on dislocations and sometimes on stacking-faults, and more particularly on intersections between the two (figure 10, a to c). The platelets nucleate with a 2-3 ° misorientation away from the matrix {III} planes and tend to become distorted

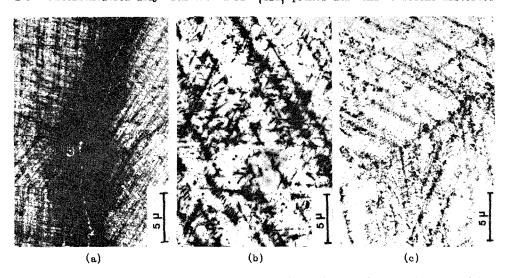
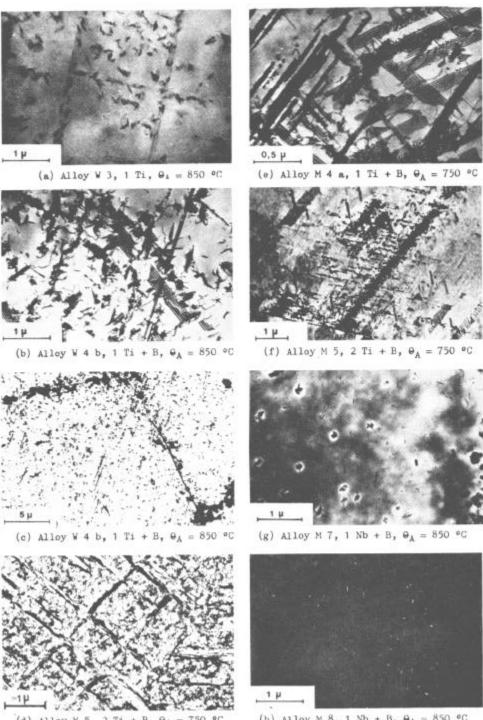


Figure 9 - Mo-containing matrix, replicas. Heat treatment 2 h 1 200 °C WQ + 16 h 750 °C AC - (a) and (b) without boron, alloy M 1 (c) with boron, alloy M 2

as they grow. Grain boundary carbides are predominantly M23C6 as is the case in all of the alloys studied. Increasing the Ti content from 1 to 2 % profoundly modifies the microstructure, figure 10 d. Fine spherical precipitates of Y' (Ni, Co)3Ti with Ll₂ structure are observed, together with lath-shaped particles identified by electron diffraction as a DO19 structure, probably Co3Ti. Small amounts of TiC and M7C3 were also detected by X-ray diffraction. The addition of 1 or 2 % Ti to the Mo-containing matrix produces structures similar to that obtained in the alloy with W and 1 % Ti, figure 10 e and f, namely TiC precipitation on dislocations. However, the secondary precipitation is less abundant, particularly in the case of 2 % Ti, for which the primary carbides are more numerous. In both matrices with 1 % Nb additions, NbC has been detected as a constituent of X-ray diffraction residues, together with M6C and M23C6. The alloys containing W and Nb have so far not been examined by electron microscopy due to the difficulty in obtaining satisfactory thin films or replicas. This problem did not arise in the case of the Mo-containing matrix in which the secondary carbides, precipitated on dislocations and particularly abundant around primary M6C particles, are of two types, $M_{23}C_6$ of $\sim 1~000$ to 2 000 Å in diameter and NbC in the form of fine platelets about 200 A in thickness, figure 10, g and h. Very few stacking faults were observed in this case.

Discussion

It has been shown that considerable variations in both aging response and in creep strength can be produced in cobalt-base matrices by means of minor alloying additions combined with suitable heat-treatments. Small boron additions, of the order of 50 to 100 ppm, systematically increase the creep resistance, but in general have no clear effect on the microstructure or hardness. In the one exception to this rule, that is, the straight W-containing matrix, addition of boron leads to a pronounced increase in secondary carbide precipitation during aging, following rapid cooling from the solution treatment temperature. The observation of abundant dislocation loops, which appear to serve as nuclei for precipitation, together with broad denuded



(d) Alloy W 5, 2 Ti + B, Θ_A = 750 °C (h) Alloy M 8, 1 Nb + B, Θ_A = 850 °C Pigure 10 - Microstructure of alloys with Ti and Nb; heat-treatment 2 h 1 200 °C WQ + 16 h Θ_A °C AC; (a) to (d) matrix with W, (e) to (h) matrix with Mo; (a) (b) (e) (f) (g) (h) thin foils, (c) (d) replicas. Micrograph (h) is the dark field image of micrograph (g) using an MC reflection. All other thin foil micrographs are bright field images

zones at the surface and at grain boundaries, suggests that boron influences the retention of vacancies. In the other alloys, precipitation takes place on dislocations and/or stacking faults. In this case boron must affect the creep strength more directly, perhaps via reduced grain boundary diffusion rates for example, but this point remains to be clarified.

The much heavier precipitation of $M_{23}C_6$ carbides in the straight Mo-containing matrix compared with that in the corresponding alloy with W may be due, at least partly, to the higher carbon content (0.2% instead of 0.1%). The difference in carbon levels is probably also the main reason for the increase in as-solution-treated hardness in the W-containing materials with Ti and Nb additions relative to the plain matrix, since the equivalent alloys with Mo, which all have $\sim 0.2\%$ C, have closely similar hardnesses before aging.

The addition of 1 % Ti replaces intragranular $M_{23}C_6$ by TiC in both matrices, whereas 1 % Nb is insufficient to eliminate completely the more complex carbide. In this respect it should be noted that the experimental alloy analyses give Nb: C ratios between 5.3 and 6.8 compared with 7.7 for the stoCchiometric NbC composition (10.3 if the composition is taken as Nb_4C_3). While the Mc carbides represent a smaller volume fraction than that of $M_{23}C_6$, the particle size is much finer and more stable at higher temperatures. Precipitation probably continues during creep since an initial period of contraction was often observed in high temperature tests.

Raising the Ti addition to 2 % led to replacement of MC carbides by intermetallic phases in the W-containing matrix and to an increase in the number of primary MC carbides at the expense of fine secondary precipitates in the alloy with Mo, the creep strength at high temperature being reduced in both cases.

Conclusions

It is possible, by means of additions of boron and MC carbide formers, combined with suitable heat treatment, to obtain considerably increased creep strengths in Co-base superalloy matrices. It is thought that further improvements could be obtained by optimisation of heat-treatment and by carefully balancing Ti or Nb: C ratios in order to approach more closely the stocchiometric MC or M_4C_3 compositions, as has been shown elsewhere in Nb and Ti-stabilised austenitic steels (4, 5). One of the compositions described in the present paper (W + 1 % Ti + B) has been investigated more thoroughly. It has been developed on an industrial scale and has successfully undergone test-bed trials in the form of a primary nozzle convergent component for the Olympus 593 Concorde engine (6, 7).

References

- 1. C. ROGISTER, D. COUTSOURADIS, L. HABRAKEN, Cobalt, 1967, nº 34, p. 3.
- 2. J. H. DAVIDSON, Y. HONNORAT, Unpublished work.
- J. H. DAVIDSON, P. BALLADON, Y. HONNORAT, X. WACHE, Mém. Sci. Rev. Mét., 1973, vol. 70, p. 543.
- 4. S. R. KEOWN, F. B. PICKERING, "Creep strength in steels and high temperature alloys", The Metals Society, London, 1974, p. 134.
- 5. T. M. WILLIAMS, D. R. HARRIES, ibid., p. 152.
- 6. J. H. D//IDSON, Rev. Mét., 1974, vol. 71, p. 943.
- 7. J. H. DAVIDSON, Matériaux et Techniques, 1975, vol. 63, p. 227.