COTAC 744 : AN OPTIMIZED D.S.
COMPOSITE FOR TURBINE BLADES

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The directionally solified composite Cotac 744, is shown to possess the overall properties required for an advanced aircraft turbine blade alloy. The development of this composite is a direct consequence of optimized mechanical properties in conjunction with good thermal stability, good oxidation behaviour and a satisfactory corrosion resistance.

A very original feature of this composite is that the heat-treatments after creep, not only permit the restoration of its creep strength but also allow the recovery of the initial length. This phenomenon, which was designated as the "Length memory effect", is evidently of substantial interest to the engine designer. The high cycle and low cycle fatigue behaviour of the uncoated and coated alloy at 650° C is found to be good. During temperature-cycled creep the maximum temperature of this composite in service, is estimated to be around 1150° C. The environmental resistance of the bare alloy is satisfactory. However, despite the good corrosion resistance of the newly developed ONERA coating, its high temperature oxidation resistance requires further improvement.

INTRODUCTION

High strength directionally solidified composites for turbine blade applications have been the subject of substantial research and development efforts during the past few years. A few promising candidate materials were identified showing improved mechanical properties over the currently employed conventional superalloys and have already been thoroughly reviewed (1, 2). However, despite their good creep strength most of these high temperature composites also have some serious drawbacks such as poor environmental resistance and / or unsatisfactory thermal stability ; the slow processing rates are unfortunately common to all the advanced eutectic systems. The purpose of this paper is to show that through a sustained research effort at ONERA, it has been possible to reach a reasonably good compromise between the various properties in order to meet the extremely stringent requirements of a candidate alloy for advanced turbine blades. This work will describe some of the salient features of a recently developed and optimized γ/γ' — NbC composite designated as Cotac 744 which is shown to possess an interesting blend of properties such as good mechanical strength, excellent structural stability and a satisfactory oxidation and corrosion resistance.

CONCEPTION OF STRUCTURALLY STABLE COMPOSITE COTAC 744

This composite was derived from the structurally stable base-line γ/γ' — NbC eutectic, Cotac 74 the properties of which have been discussed elsewhere (3). Considerable alloy development work was carried out at ONERA to improve the stress rupture properties of Cotac 74 through compositional modifications. These refinements mainly consisted in increasing the aluminium content to obtain a higher volume fraction of γ' precipitates and lowering the cobalt content while maintaining a reasonably high concentration of refractory elements. During these compositional adjustments it was realized that in some of the alloys having a high volume fraction of γ' the NbC fibers transformed to $M_{23}C_6$ particles at intermediate temperatures (700—1000°C). A systematic study of the structural stability of γ/γ' — NbC composites was therefore initiated which revealed that the structural transformation of the reinforcement is primarily dependent upon the chromium and the aluminium contents. A three phase region (γ, NbC, $Cr_{23}C_6$) was determined in simple Ni—Cr—NbC composites in the temperature range 700—1000°C. A stability criterion was subsequently established for complex γ/γ' — NbC composites and their structural stability, experimentally verified (4). It was finally concluded that in these composites the fibers would remain stable if the chromium content of the γ solid solution phase is kept below 15 Wt%. Compositional adjustments and structural stability investigations led us to select the Cotac 744 composite ; the chromium content of the γ phase in this perfectly stable alloy is about 10 Wt%. The nominal compositions (Wt%) of Cotac 744 and the base-line eutectic are as follows :

Cotac 744 : Ni 10 Co4Cr 10W 2 Mo 6Al 3.8 Nb 0.47 C

Cotac 74 : Ni 20 Co 10 Cr 10 W 4 Al 4.9 Nb 0.6C

The melting point of Cotac 744 is 1340 ± 5°C and the γ' solvus, 1200°C.

The volume fractions of γ' precipitates and fibers are 60% and 6% respectively ; the density of the new alloy is 8.5. The reasonably low melting range ($\sim$ 10°C) permits directional solidification of semi-industrial ingots up to a rate of 16 mm per hour. So far as the feasibility of complex solid airfoil shapes is concerned, a promising new process designated as the "tin column process" was developed and successfully tested at ONERA (5). The mechanical test results reported in this paper were obtained on specimens solidified at a rate of 12 mm per hour. All specimens used for mechanical testing were given the following standard heat treatments :

20 minutes/1200°C/AC + 16 hours/850°C/AC on Cotac 744.

20 minutes/1100°C/AC + 16 hours/760°C/AC on Cotac 74.

TENSILE PROPERTIES

The tensile properties of Cotac 744 are compared to the base-line composite, Cotac 74 in Table 1.

Tests were performed at a cross-head speed of 0.24 mm/min. on 30-mm gauge length specimens. The new composite, Cotac 744 has much better high-temperature strength and ductility than Cotac 74. This was confirmed by performing tensile tests at an extremely slow strain rate of $5.10^{-5}h^{-1}$ on these composites at 950°C (fig. 1) ; the the strain rate is comparable to the creep rates. The Cotac 744 alloy failed in a ductile manner after 8% strain whereas Cotac 74 failed in a brittle manner after about 1% strain;

Table 1. Tensile properties of Cotac 744 and Cotac 74.

Alloy	COTAC 744		COTAC 74	
tensile proper-ties (°C) temperature	U.T.S. (MPa)	Elongation (%)	U.T.S. (MPa)	Elongation (%)
25	1505	13	1505	12.4
800	1170	12	1000	7
900	910	10	680	7.7
950	680	15	580	7
1000	570	10	415	6.6
1070	406	11	287	5

Fig. 1. Stress—strain curves at a very slow strain rate.
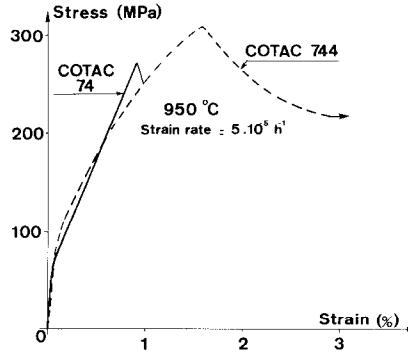
the total time to failure for Cotac 744 and Cotac 74 was 660 hours and 210 hours re-spectively. It is interesting to notice that the fiber failure stress at such slow strain rates is almost 2.5 times lower than in a standard tensile test.

CREEP BEHAVIOUR

STRESS—RUPTURE PROPERTIES

The density-corrected stress rupture strength of the uncoated Cotac 744 is compared to the base-line eutectic Cotac 74 and DS200 + Hf superalloy in fig. 2. The improvement offered by Cotac 744 over Cotac 74 and the DS200 superalloy is clearly shown in this figure. Although the intermediate temperature strength of the new eutectic is close to the superalloy, this composite shows a considerable improvement in the high-temperature high-stress regime.

The creep curves of Cotac 744 show distinct primary, steady state and tertiary re-gions. The steady-state creep rate in the temperature range 800-1070°C is well represen-ted by the relationship $\dot{\epsilon}_s = A \sigma^n$; the value of the stress exponent is close to 11.

The elongation before rupture is high up to 1000°C (4-10%) but failure usually oc-curs around 2% strain beyond this temperature.

coating can have a deleterious effect on the otherwise exellent fatigue strength of a eutectic. Moreover, it was desirable to study the effect of testing frequency on the coated alloy since most aluminide coatings have a relatively low ductility up to at least 650°C. Prior to reporting the fatigue results it is useful to recall the monotonic stress-strain behaviour of the alloy at 650°C : the matrix yields at about 750 MPa, the fiber failure and the associated load drop occur at 1140 ± 10 MPa; the U.T.S. is around 1360 MPa.

TENSION—TENSION TESTS

Tests were performed on hour-glass specimens in the longitudinally ground condition using the load controlled mode and a sine waveform. The fatigue response of the uncoated and coated eutectic was first studied at a low frequency (0.1 Hz) and then under high frequency conditions (20—35 Hz) to provide a broader framework for evaluating the fatigue properties of Cotac 744. The minimum stress was always 1/10th of the maximum stress which gives a constant "A ratio" (alternating stress / mean stress) of 0.818. If the maximum stress (σ_{max}) is 1120 MPa or less, the specimens do not fail before 50 000 cycles and post—test metallography did not reveal any fiber rupture. Confirmation of the integrity of fibers was obtained by performing creep tests at 850 and 1000°C on specimens previously cycled up to 50 000 cycles; the rupture lives were as long as those obtained on virgin creep specimens. It is clear that no fatigue damage is occuring in these conditions. Tests were now continued on coated specimens at the same frequency. Two aluminide coatings were used : a well known industrial coating, the so-called "Chromaluminization" (H1—15) deposited by Heurchrome and an experimental ONERA coating designated as F7G which is shown to possess good corrosion resistance in a later section of this paper. After the standard heat treatment, the final coating thickness was approximately 55 µm. The fatigue tests showed that fiber failure did not occur in 5.10^4 cycles if σ_{max} is below 1060 MPa on chromaluminized specimens and below 960 MPa on the F7G—coated alloy. Nonetheless, all specimens contained very fine cracks in the coating (fig. 3). The metallographic examinations indicated that the cracks initiate after at least 1000 cycles in the external layer of the coating and invariably stop at the coating-substrate interface, provided that σ_{max} is lower than 1060 MPa in the case of chromaluminized alloy and below 960 MPa for the F7G—coated specimens.
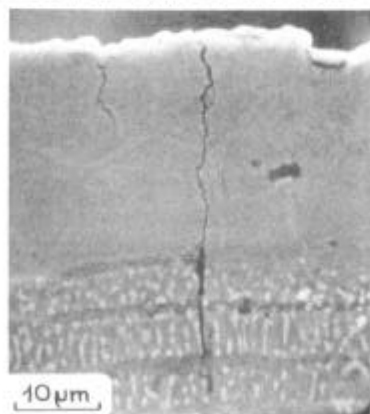

Fig. 3. Fatigue cracks exclusively in the coating of chromaluminized samples after 54 500 cycles (σ_{max} = 1060 MPa; frequency = 0.1 Hz).

Tension-tension tests were continued at $650°C$ to determine the 10^7—cycle fatigue limit of both the uncoated and the coated alloy using higher frequencies (20 to 35 Hz). A clearly defined fatigue limit does exist in Cotac 744 around a σ_{max} value of 1000 MPa regardless of the frequency. A previous study on Nitac 13 reported a correlation between the fatigue limit and the matrix yield stress (8). This is in contrast to the observations on Cotac 744 where the fatigue limit is much higher (1000 MPa) than the matrix yield stress ($\sim$ 750 MPa). An interesting observation which is worth mentioning here is that if the specimens are subjected to 10^7 cycles at a σ_{max} slightly below the fatigue limit and subsequently tensile tested at $650°C$, the fiber failure stress is raised from 1130 to 1290 MPa showing a very substantial work hardening of the matrix.

The H.C.F. life of coated specimens is significantly affected by the high loading rates associated with high frequencies on a rather brittle coating. The cracks initiate in the coating extremely rapidly. Hence at a σ_{max} of 900 MPa the chromaluminized specimens tested at 35 Hz failed in about 15 000 cycles whereas at 0.1 Hz the coated eutectic did not fail after 50 000 cycles even at a σ_{max} of 1060 MPa. The fatigue limit of chromaluminized alloy is however, still very high (800 MPa).

TENSION—COMPRESSION TESTS

The tension-compression fully reversed L.C.F. tests were performed under longitudinal strain control at $650°C$ using a frequency of 0.1 Hz on uncoated and chromaluminized specimens : the results are plotted in Fig. 4. The uncoated specimens do not fail in 50 000 cycles if the corresponding stabilized stress is below 750 MPa. The L.C.F. response of Cotac 744 is comparable to the D.S. MAR246 superalloy. The Coffin-Manson correlation for plastic strain, $N_f^\alpha \Delta\epsilon_p$ = constant seems to be moderately good but more results are needed to confirm a better fit. Although the chromaluminized specimens have shorter lives, the damaging effect of this coating is by no means serious. However, further work is required to assess the effect of the experimental F7G—coating which is less ductile as observed during the tension-tension tests. Transmission electron microscopy observations were undertaken on uncoated specimens fatigued both in tension-tension and tension-
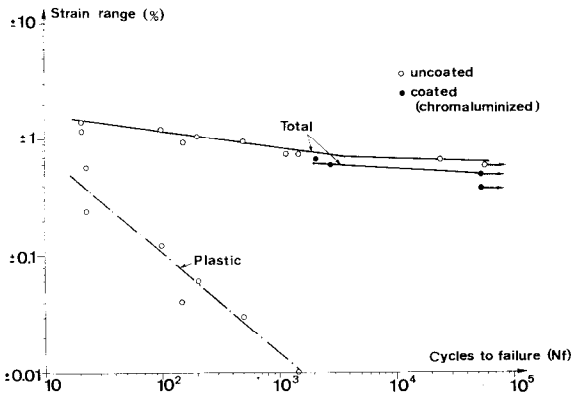

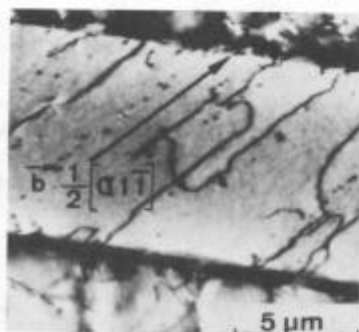Fig. 4. Low cycle fatigue curves of Cotac 744 at $650°C$.

Fig. 5. Typical slip dislocations in NbC
fiber after tension-compression fatigue.
(Strain range = ± 0.76% ; N_f = 1550).

compression. In tension-tension tests perfor-
med at 0.1 Hz, if σ_{max} is high (but below
the fiber failure stress) the matrix is heavily
deformed but the fibers were not found to
contain dislocations. On the contrary, the ten-
sion-compression specimens often revealed slip
dislocations (predominantly screw) within the
fibers (Fig. 5). Whether the presence of these
dislocations would influence the subsequent
creep behaviour of the eutectic is not yet
clear; one would expect a degradation of pro-
perties only if there is a possibility of disloca-
tion multiplication within the fibers.

THERMAL CYCLING

The thermal cycling behaviour of Cotac composites has been analyzed and discussed
in terms of the generation of cumulative plastic strains in the matrix which subsequently
lead to fiber degradation (3). It was further shown that during thermal cycling the matrix
is constantly subjected to thermal fatigue in tension-compression. It became therefore
clear that if the matrix of the composite has a high strength, the fiber degradation can be
avoided up to a high temperature. As regards the Cotac 744 composite, 2500 cycles of
3-minute duration between 1150°C and 250°C did not result in any visible fiber damage.
However, in temperature cycled creep with a 30-minute cycle period (28 minutes hold
time at 1150°C) and a stress of 40 MPa some fiber degradation did occur after 2500 cyc-
les. Various metallographic examinations seem to indicate that the maximum temperature
for the use of this composite is close to 1150°C i.e. about 50°C higher than that for
Cotac 74.

OXIDATION AND CORROSION RESPONSE OF BARE
AND COATED COMPOSITE

Cyclic oxidation tests were performed on uncoated cylindrical specimens using a
one-hour cycle period and rapid air cooling. The specific weight change curves of Cotac
composites and IN100 superalloy at various temperatures are shown in Fig. 6 after 400
cycles. It is apparent that Cotac 744 (with or without yttrium) which has a high alumi-
nium content (6%) is more oxidation resistant than Cotac 74 (4% Al). Minor yttrium ad-
ditions (0.2%) substantially improve the cyclic oxidation behaviour of Cotac 744. Parallel
to these studies, the effect of fiber orientation relative to the surface, upon the oxidation
response of Cotac 744 was considered. Uncoated coupon samples with fibers either para-
llel or normal to the surface were tested in both isothermal and cyclic oxidation at 1050°
and 1100°C : specimens with fibers perpendicular to the surface showed a significantly
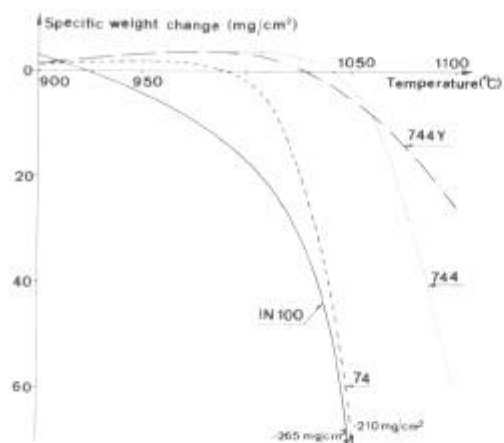higher weight gain in isothermal tests and higher weight loss in cyclic oxidation.

Fig. 6. Specific weight change curves for Cotacs 744, 744Y, and IN100 in cyclic oxidation (400 cycles).

The hot corrosion tests were run at $850°$ and $950°C$ in the SNECMA burner rig on bare Cotac composites (744, 744Y, 74) and IN100. The test duration was fixed to be 500 hours. At $950°C$ all alloys completed the 500—hour test; metallographic examinations revealed that the corrosion attack was only 15–30 µm deep. At $850°C$ however, only Cotac 744Y and Cotac 74 completed the test duration; the IN100 superalloy and Cotac 744 were removed from the rig after 150 hours and 350 hours respectively. The corrosion attack at $850°C$ was limited to about 20 µm in the Cotac alloys but attained 350 µm in IN100. The anisotropic behaviour of Cotac 744 was again observed in corrosion tests above $850°C$. The penetration depth of corrosion products is four times higher in the longitudinal direction due to preferential oxidation of fibers (Fig. 7).Inspite of its low chromium content the corrosion behaviour of Cotac 744 is much better than that of IN100 superalloy. As regards the protective coatings, the standard aluminizing techniques applied to fiber reinforced Cotac composites do not guarantee sufficient protection against agressive environments because of internal oxidation of fibers and the presence of pores. The experimental "F7G" coating consists in the insertion of an intermediate carbide—free layer and subsequent aluminizing. Corrosion tests in the SNECMA burner rig
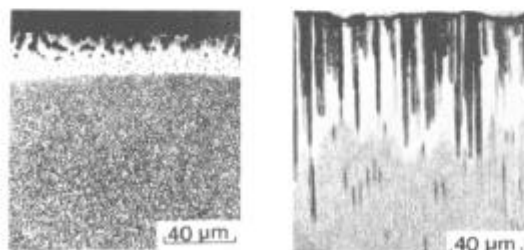

Fig. 7. Burner rig corrosion test at $950°C$ / 500 h showing preferential oxidation parallel to fiber orientation.

with 5 ppm salt in the combustion gas were performed on the F7G coated Cotac 744 and the chromaluminized IN100. Both at 850° and 950°C where corrosion is predominant, the F7G coated alloy showed good resistance in the 500—hour test whilst the chromaluminized IN100 suffered severe corrosive attack after 300 hours. Metallographic examination of the coated composite revealed that only 50% of the coating thickness was consumed after 500 hours. At 1050°C however, where oxidation is predominant the composite had a poor response compared to the coated IN100 and it was therefore removed from the rig after 400 hours. The coated IN100 was apparently not damaged even after 500 hours.

CONCLUSIONS

The high strength Cotac 744 composite is an interesting candidate material for advanced turbine blades due to a good compromise between its mechanical strength, structural stability and environmental resistance. A unique feature of this composite is that a few periodic heat treatments would not only restore the creep strength of rotating blades but also permit the recovery of their initial length. This phenomenon has been termed as the "length memory effect" and is clearly of considerable interest to the engine designer. The slow processing rates in the case of this composite could be offset by the prolonged rupture lives obtained through a few re-heat-treatments. Both the H.C.F. and L.C.F. response of chromaluminized (H1—15 coated) composite is good at 650°C; the F7G coating has not yet been evaluated in L.C.F. This recently developed ONERA coating, despite its good corrosion resistance needs further improvement in terms of its oxidation resistance at high temperatures.

ACKNOWLEDGMENTS

REFERENCES

(1) H. Bibring, AGARD CP 229, 1978.

(2) N. S. Stoloff, CISC—III, Boston, Nov. 29 — Dec. 1, 1978, p. 357.

(3) H. Bibring, T. Khan, M. Rabinowitch and J. F. Stohr, Proc. of the Third International Symposium, Seven Springs, Sept. 12 — 15, 1976, p. 331.

(4) J. F. Stohr, CISC—III, Boston, Nov. 29 — Dec. 1, 1978, P' 130.

(5) M. Rabinovitch and J. M. Hauser, CISC—III, Boston, Nov. 29 — Dec. 1, 1978, p. 246.

(6) T. Khan, CISC—III, Boston, Nov. 29 — Dec. 1, 1978, p. 378.

(7) T. Khan, To be published in Materials Science and Engineering.

(8) D. E. Graham and D. A. Woodford, Met. Trans. A, Vol. 10 A, Sept. 1979, p. 1303.

(9) C. A. Bruch, R. W. Harrison, M. F. X. Gigliotti, M. F. Henry, R. C. Haubert and C. H. Gay, CISC—III, Boston, Nov. 29 — Dec. 1, 1978, p. 258.