COBALT-FREE NICKEL-BASE WROUGHT SUPERALLOYS

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A study has been made of the influence of C, Cr, Co, Mo, W, Ta, Al, Mn, Si and Y on the high temperature oxidation resistance of a group of experimental nickel-base superalloys. Oxidation was performed in flowing air at 1095 C (2000 F) with intermittent cycling to room temperature. Al additions increased resistance to oxide spalling, and Y additions limited both total mass gain and oxide spalling. Mo and W additions improved resistance to both mass gain and oxide spalling. Synergism between Si and each of the elements Ta, Y and Al promoted oxide spalling. Co was not essential for adequate oxidation resistance. Stress rupture properties similar to those of cobalt-base Haynes Alloy 188 and of Inconel 617 (12.5% Co) at 870 C (1600 F) and 1095 C (2000 F) were achieved with a cobalt-free alloy.

INTRODUCTION

The current restricted supply and high cost of cobalt has led to an increased interest in the development of cobalt-free superalloys. No cobalt-free wrought solid solution strengthened superalloy with properties equivalent to those of cobalt-base Haynes Alloy 188 (1) or Inconel 617 (2) containing 12.5% Co, is currently available. The present study was directed towards the development of such an alloy and, accordingly, has evaluated the high temperature oxidation resistance, and to a more limited extent, the stress-rupture properties, of a group of experimental nickel-base alloys.

EXPERIMENTAL PROCEDURES

The nominal compositions of the alloys evaluated in this

study are shown in Table 1. The alloys in Group A represent a 1/4 replicate of a 2^6 factorial design, those in Group B represent a 1/2 replicate of a 2^5 factorial design, and those in Group C represent a 1/2 replicate of a 2^4 factorial design. These designs provide information on the main effects and two-element interaction effects, either separately or in combination, for the elements varied.

The alloys in Groups A, B, and C were prepared from 100-250 g lots of blended elemental powders that were arc-melted into small ingots in an argon atmosphere. Groups A and B ingots were homogenized at 1260 C (2300 F), and Group C ingots at 1230 C (2250 F), for 8 hours in hydrogen. Group A ingots were forged at 1150 C (2100 F) to a thickness of 5 mm (0.2 in.), Group B alloys were studied in the homogenized condition and Group C alloys were hot rolled at 1205 C (2200 F) to 1.5 mm

Table 1 Nominal Alloy Compositions (wt %)

Alloy	C	Mn	Si	Cr	Ni	Co	Mo	W	Ta	Al	Y	B	Zr
A- 1	0.1	-	-	20	Bal	4	8	2	2	1	-	0.01	0.08
2	0.2	-	-	20	Bal	4	8	6	2	1	-	0.01	0.08
3	0.1	-	-	25	Bal	4	8	6	6	1	-	0.01	0.08
4	0.2	-	-	25	Bal	4	8	2	6	1	-	0.01	0.08
5	0.1	-	-	20	Bal	10	8	6	6	1	-	0.01	0.08
6	0.2	-	-	20	Bal	10	8	2	6	1	-	0.01	0.08
7	0.1	-	-	25	Bal	10	8	2	2	1	-	0.01	0.08
8	0.2	-	-	25	Bal	10	8	6	2	1	-	0.01	0.08
9	0.1	-	-	20	Bal	4	12	2	6	1	-	0.01	0.08
10	0.2	-	-	20	Bal	4	12	6	6	1	-	0.01	0.08
11	0.1	-	-	25	Bal	4	12	6	2	1	-	0.01	0.08
12	0.2	-	-	25	Bal	4	12	2	2	1	-	0.01	0.08
13	0.1	-	-	20	Bal	10	12	6	2	1	-	0.01	0.08
14	0.2	-	-	20	Bal	10	12	2	2	1	-	0.01	0.08
15	0.1	-	-	25	Bal	10	12	2	6	1	-	0.01	0.08
16	0.2	-	-	25	Bal	10	12	6	6	1	-	0.01	0.08
B- 1	0.1	-	-	20	Bal	4	8	6	2	-	-	0.01	0.08
2	0.1	0.5	-	20	Bal	4	8	6	2	1	-	0.01	0.08
3	0.1	-	-	20	Bal	4	8	6	6	1	-	0.01	0.08
4	0.1	0.5	-	20	Bal	4	8	6	6	-	-	0.01	0.08
5	0.1	-	0.5	20	Bal	4	8	6	2	1	-	0.01	0.08
6	0.1	0.5	0.5	20	Bal	4	8	6	2	-	-	0.01	0.08
7	0.1	-	0.5	20	Bal	4	8	6	6	-	-	0.01	0.08
8	0.1	0.5	0.5	20	Bal	4	8	6	6	1	-	0.01	0.08
9	0.1	-	-	20	Bal	4	8	6	2	1	0.1	0.01	0.08
10	0.1	0.5	-	20	Bal	4	8	6	2	-	0.1	0.01	0.08
11	0.1	-	-	20	Bal	4	8	6	6	-	0.1	0.01	0.08
12	0.1	0.5	-	20	Bal	4	8	6	6	1	0.1	0.01	0.08
13	0.1	-	0.5	20	Bal	4	8	6	2	-	0.1	0.01	0.08
14	0.1	0.5	0.5	20	Bal	4	8	6	2	1	0.1	0.01	0.08
15	0.1	-	0.5	20	Bal	4	8	6	6	1	0.1	0.01	0.08
16	0.1	0.5	0.5	20	Bal	4	8	6	6	-	0.1	0.01	0.08
C- 1	0.05	0.5	-	20	Bal	8	4	6	6	2	0.2	0.01	0.08
2	0.08	0.5	-	20	Bal	8	4	6	9	2	0.2	0.01	0.08
3	0.05	0.5	-	20	Bal	8	8	6	9	2	0.2	0.01	0.08
4	0.08	0.5	-	20	Bal	8	8	6	6	2	0.2	0.01	0.08
5	0.05	0.5	-	20	Bal	8	4	9	9	2	0.2	0.01	0.08
6	0.08	0.5	-	20	Bal	8	4	9	6	2	0.2	0.01	0.08
7	0.05	0.5	-	20	Bal	8	8	9	6	2	0.2	0.01	0.08
8	0.08	0.5	-	20	Bal	8	8	9	9	2	0.2	0.01	0.08
D[a]-1	0.08	0.5	0.1	20	Bal	-	9	9	3	1	0.05	0.005	0.05
2	0.05	0.5	0.1	20	Bal	-	5	5	2	1	0.05	0.005	0.05
Inconel 617[b]	0.08	0.1	0.2	20.4	Bal	11.5	8.4	-	-	0.8	-	-	-
Haynes Alloy 188[c]	0.10	0.7	0.4	22.9	22.4	Bal	-	14.8	-	-	-	-	-

[a] Group D alloys contain 0.2% Ti. [b] Inconel 617: Heat No. XX01A1 U5
[c] Haynes Alloy 188: Heat No. 1880-4-1698 (containing 1.2Fe, 0.07La)

(0.06 in.) thick sheet. The Group D alloys were vacuum melted
and cast as 30 kg heats, extruded at 1150 C (2100 F) with an
extrusion ratio of 4 and then hot rolled at 1205 C (2200 F) to
1.5 mm (0.06 in.) thick sheet. Sheet samples of similar thick-
ness from commercial heats of Inconel 617 and Haynes Alloy 188
were used in the oxidation studies for reference purposes, and
the compositions of these heats are appended to Table 1. Spec-
imens for oxidation studies were polished through 600 grit
paper, cleaned and weighed, then oxidized in flowing air for up
to 420 hours at 1059 C (2000 F), using a flow rate of 100 cm^3/
sec. Specimens were cooled to room temperature at regular in-
tervals to promote oxide spalling and to permit weighing. Mass
gain and mass of spalled oxide were measured at each weighing.

RESULTS AND DISCUSSION

Group A Alloys

Oxidation. The specific mass changes that occurred during
the oxidation of the Group A alloys were recorded. Duplicate
specimens of Alloys A-9 and A-12 were exposed and indicated
acceptable reproducibility for the test. The total mass changes
for all the Group A alloys were greater than those exhibited by
Inconel 617 and Haynes Alloy 188 indicating the necessity for
compositional modifications to the experimental alloys.

The identity of elements that were most effective in con-
tributing to the observed oxidation behavior was determined
from statistical analysis (3) of the mass gain and mass loss
data at the end of the oxidation exposure. Based on previous
laboratory experience, standard deviations of ±10% of the mean
mass gain and of ±1 mg cm^{-2} for the spalled oxide data were
considered appropriate in identifying mean squares that were
significant at a 90% level of confidence. The elements thus
identified as influencing the oxidation resistance of the Group
A alloys after 420 hours of exposure are listed in Table 2.
The tabulated coefficient associated with each element indicates
the magnitude of the effect on both mass gain and oxide spall-
ing, in mg cm^{-2}, caused by changing that element from its lower
to its higher level. A negative sign associated with a coeffi-
cient indicates that mass gain or spalled oxide is decreased by
the change in composition, which is equivalent to an increase
in oxidation resistance.

Table 2 indicates that oxidation resistance in the Group
A range of compositions is increased by the increase in Mo and
W contents and is decreased by the increase in Ta content. The
mass of oxide spalled is decreased by the W and Co additions

Table 2   Group A Coefficients

Element	Mass Gain	Mass Loss
Co	–	-2.18
Cr	–	+0.92
Mo	-1.68	–
W	-0.90	-1.14
Ta	+1.65	+4.4
CrCo+CW+MoTa	–	-0.90

and by one or more of the two-element interactions combined in the (CrCo + CW + MoTa) confused interaction effect, and is increased by the increases in Ta and Cr content.

These mass change data indicated that oxidation resistance was decreased by the increase in Ta content. Since Ta had been included in the alloys to increase solid solution strengthening, its retention at the 2% level on the basis of this initial oxidation study was clearly premature. The design of the Group B alloy compositions was, therefore, formulated by using minor additions of Mn, Si, and Y to improve oxidation resistance while retaining Ta at its former levels.

The increases in Co from 4% to 10%, in Mo from 8% to 12% and in W from 2% to 6% in the Group A alloys were beneficial in increasing oxidation resistance. At the same time, the phase stability aging treatment of these alloys led to the precipitation of μ phase in alloys A-3 to A-16. Therefore it was clear that lower levels of the μ-forming elements should be used in the next phase of the study while retaining emphasis on elements that would provide maximum solid solution strengthening. Accordingly the lower levels of Cr, Co, and Mo were used in the design of Group B alloy compositions, together with the upper W level.

Group B Alloys

Oxidation Study. The mass changes observed for the Group B alloys were recorded. Oxidation was protective to varying degrees for all alloys, and the mean mass gain for the alloys at any specific time was less than the mean gain at the same time for the Group A alloys. Thus the alloy modifications had achieved the desired effect of decreasing the extent of oxidation. However the degree of oxide spalling was much greater than that recorded for the Group A alloys, indicating need for further compositional modification.

Statistical analysis of the mass gain and spalled oxide data after 400 hours exposure was performed as before. The elements identified as influencing the oxidation resistance of

Table 3 Group B Coefficients for Significant Effects After
Oxidation at 1095 C (2000 F) for 400 Hours

Element	Mass Gain	Mass Loss	Element	Mass Gain	Mass Loss
Al	-0.48	-5.06	SiTa	–	+6.59
Mn	-0.78	-4.61	SiAl	–	+6.11
Si	-0.50	–	SiY	+0.70	+3.89
Ta	-0.65	-3.04	SiMn	–	-1.91
Y	-0.92	-3.64	TaY	–	+3.24
AlY	-1.42	-5.06	TaAl	–	+1.91
MnY	+0.52	-3.24	TaMn	–	+1.16

the alloys are listed in Table 3 together with their respective
coefficients. Table 3 indicates that mass gain is diminished
by the specified increases in Al, Mn, Si, Ta, and Y, and by a
strong synergism between Al and Y. Synergism between Si and Y,
and Si and Ta, leads to increases in mass gain. Oxide spalling
is decreased by the increases in Al, Mn, Ta and Y, and by syner-
gism between Al and Y, Mn and Y, and Mn and Si. Oxide spalling
is increased by synergistic interactions between Si and Y, Si
and Al, Si and Ta, Ta and Y, Ta and Al, and Ta and Mn. Evident-
ly the increases in both Si and Ta contents in these Group B
alloys give rise to a marked decrease in resistance to oxide
spalling in the presence of both Al and Y, although in isolation
Ta contributes towards an increase in resistance to spalling.

The most oxidation-resistant arc-cast alloy at this stage
of the study was Alloy B-12. The scale was composed predominant-
ly of Cr_2O_3, with Y-rich particles extending into the matrix
below the scale. The oxidation resistance of this alloy ap-
proached that of the Inconel 617 sample in this test.

The information gained on alloying effects was then com-
bined in the design of the Group C alloy compositions. The
composition of Alloy B-12 was used as a guide in developing the
alloy group. Low carbon levels were used to minimize the ten-
dency for the formation of large blocky carbides during casting
that could decrease LCF resistance. Both Al and Y were retained
and were increased to 2% and 0.2%, respectively, in an attempt
to gain further increases in oxidation resistance over that of
the Group B alloys. Cr was maintained at 20% and Co was in-
creased to 8% to gain some further increase in spalling resis-
tance. The concentrations of Mo, W, and Ta were chosen to pro-
vide maximum solid solution strengthening in addition to oxida-
tion resistance, with emphasis being placed on W and Ta, the
elements with larger atomic diameters. Thus Mo was varied be-
tween 4% and 8%, and W and Ta were each varied from 6% to 9%.
It was recognized that several of the more highly alloyed com-
positions would be unstable with respect to TCP phase precipi-
tation.

(a)   (b)
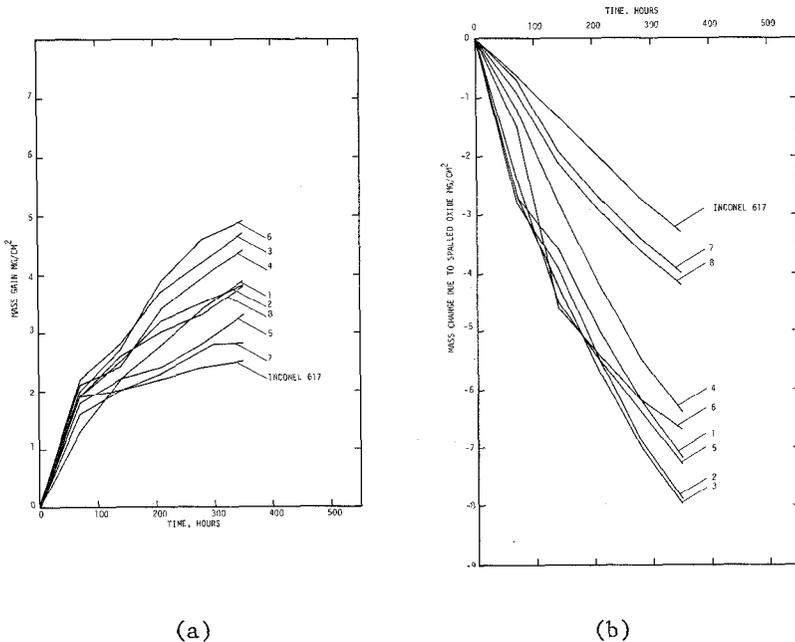
Fig. 1   Specific Mass Changes of Group C Alloys.   a) Mass gain,
         b) Mass loss due to spalled oxide.

Group C Alloys

Oxidation Study.   The mass change data for the Group C
alloys are shown in Figure 1.   These alloys exhibited a general
improvement in oxidation resistance over that of the two pre-
vious alloy groups.   A major improvement in resistance to oxide
spalling was evident, with Alloys C-7 and C-8 exhibiting greater
overall spalling resistance than Alloy B-12.   Thus these two
compositions approached an optimum composition for oxidation
resistance under the laboratory test conditions.   The closest
approach to the oxidation resistance of Inconel 617 was ex-
hibited by Alloy C-7.

     Statistical analysis of the mass changes data after 350
hours exposure yielded the set of coefficients listed in Table
4 for those elements that influenced the oxidation resistance
of the alloys.   Table 4 indicates that mass gain is diminished
by the combined interaction (CTa + MoW) but is increased by the
increase in carbon content and by the combined interaction
(CW + MoTa).   Oxide spalling is decreased by the increases in
Mo and W and by the combined interaction (CTa + MoW).   Neither

Table 4 Group C Coefficients

Element	Mass Gain	Mass Loss
C	+0.55	–
Mo	–	-1.62
W	–	-1.82
CW+MoTa	+0.75	–
CTa+MoW	-0.50	-1.28

changes in Ta content from 6% to 9% nor the higher Al and Y
levels appear to have influenced oxidation resistance. Alloys
with the higher Mo and W levels and the lower C levels exhibit
the best overall oxidation resistance. This observation on the
contributions of Mo and W to oxidation resistance is consistent
with the data obtained for the Group A alloys. The contribu-
tions of each two-factor interaction to the (CW + MoTa) and
(CTa + MoW) combined interaction effects recorded for the Group
C alloys cannot be isolated without further study. However, it
may be speculated that rapid oxidation of carbides and sub-
sequent scale spalling could account for the general detrimental
effect of increased carbon on mass gain and for possible detri-
mental CW and CTa synergistic interaction effects, whereas
synergism between Mo and W could account for beneficial in-
fluences on both mass gain and oxide spalling.

After aging at 870 C (1600 F) for 700 hours, M_6C carbide
and μ phase were found to have precipitated in all alloys except
Alloy C-1, in which only M_6C had precipitated. All alloys con-
tained $M_{23}C_6$ and MC carbides.

Group D Alloys

Alloy Compositions. The oxidation and phase stability
data observed in this study were synthesized in the formulation
of the compositions of the Group D alloys. Co had been observed
to improve oxide spalling resistance in the Group A alloys but
had not prevented the achievement of good oxidation resistance
in the Group B alloys when maintained at 4%. The improvement
in oxidation resistance of the better Group C alloys, approach-
ing equivalence to Inconel 617, was attributable at least in
part to their higher Mo and W contents, and the increase in Co
from 4% in the Group B alloys to 8% in the Group C alloys was
apparently not associated with an obvious improvement in oxida-
tion resistance. Thus the lower Co content Alloy B-12 (4Co,
8Mo, 6W, 6Ta) exhibited a slightly lower mass gain and an equiv-
alent mass of spalled oxide when compared with the higher Co
content Alloy C-4 (8Co, 8Mo, 6W, 6Ta). Therefore, in the
absence of a clearly defined, unique, beneficial contribution

to oxidation resistance from Co, this element was not included
in the Group D alloys. High and low levels of Mo and W were
examined. Ta was retained at a low level because, although it
would contribute to solid solution strengthening, it would also
contribute to phase instability, and the absence of a strong
contribution to oxidation resistance did not justify a high
content. As anticipated, Alloy D-1 was unstable with respect
to μ phase formation whereas Alloy D-2 was stable.

   Stress Rupture Properties. Stress rupture tests were made
on sheet samples of Alloys D-1 and D-2 following solution
treatment. Table 5 shows rupture data for tests between 870 C
(1600 F) and 1095 C (2000 F) for the indicated solution treat-
ment. High solution temperatures were required in order to
achieve grain sizes in the range ASTM No. 2-4 in the hot rolled
sheet. The data for Alloy D-2 are displayed in the Larson-
Miller curve of Figure 3 where they are contrasted with pub-
lished data for commercial Inconel 617 (4) and Haynes Alloy
188 (5). The rupture properties of Alloy D-2 at 870 C (1600 F)
and 1095 C (2000 F) approach closely the rupture properties of
the commercial alloys. This similarity in properties indicates
that the addition of Co is not essential to the achievement of
an acceptable high temperature rupture life in this alloy. The
rupture specimens tested at 980 C (1800 F) failed prematurely
due to excessive grain boundary oxidation, believed to be
associated with reduced oxidation resistance of the alloy due
to its low Y content.

Table 5 Stress Rupture Data for Group D Alloys

Alloy	Solution Treatment, C (F)/hr	Test Temperature, C (F)	Stress MPa (ksi)	Rupture Life, Hr	El., %
D-1	1260 (2300)/1	1095 (2000)	21 (3)	37.5	51
	1230 (2250)/4	1095 (2000)	21 (3)	55.1	40
D-2	1260 (2300)/1	1095 (2000)	21 (3)	41.7	48
		980 (1800)	48 (7)	9.5	39
		870 (1600)	117 (17)	45.6	14
	1205 (2200)/1	1095 (2000)	21 (3)	38.2	70
		1095 (2000)	21 (3)	26.6	62
		980 (1800)	48 (7)	9.1	44
		980 (1800)	48 (7)	8.0	40
		870 (1600)	117 (17)	68.6	20
		870 (1600)	117 (17)	44.8	15
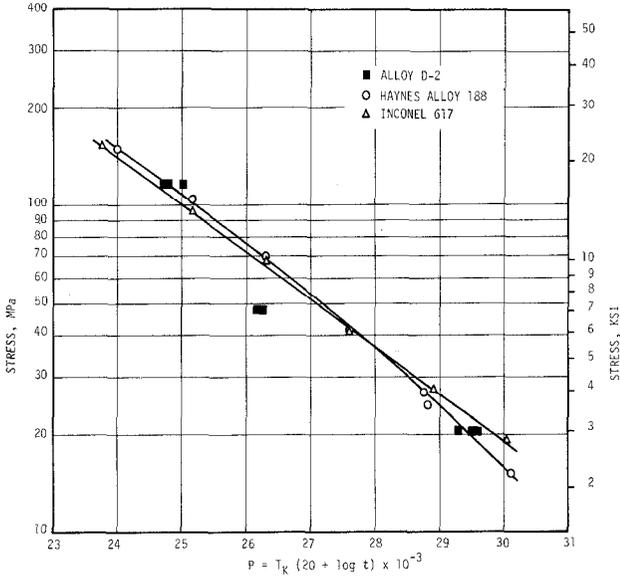
Fig. 3   Larson-Miller Parameter Plot for Rupture Lives of
Alloy D-2, Inconel 617 and Haynes Alloy 188.

CONCLUSIONS

It is clear from this work that cobalt-free nickel-base
superalloys with high temperature oxidation resistance and
stress rupture properties approaching those of cobalt-
containing commercial high temperature alloys can be developed.
The presence of significant concentrations of Mo and W is re-
quired in these Co-free alloys for the achievement of adequate
high temperature properties.

ACKNOWLEDGEMENT

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