

ROLE OF COBALT IN WASPALOY

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Nickel was systematically substituted for cobalt in Waspaloy. Mechanical test results indicate that lower cobalt has little effect on tensile properties, but adversely affects creep rate and stress rupture life. Phase extraction studies found slight decreases in gamma prime volume fractions and increased $M_{23}C_6$ carbide with lower cobalt. It is suggested that changes in gamma prime volume fraction, carbide precipitation, and stacking fault energy contribute to the decrease in creep resistance.

INTRODUCTION

Interest in the role of specific elements in the design of nickel-base superalloys has been dramatically revitalized in the past two years. Economic and strategic considerations have prompted re-examination of the necessity of raw materials whose availability could be jeopardized by political unrest or resource depletion. Recently, an element of primary concern has been cobalt, which comprises from 8-19 wt.% of some of the most commonly used wrought alloys.

Information on the role of cobalt in nickel-base superalloys was found insufficient to ascertain if the specified levels of cobalt in many commercial superalloys is justified. Therefore, a one variable study was initiated on the systematic replacement of cobalt by nickel in Waspaloy, which accounts for the greatest consumption of "nickel-base superalloy" cobalt. Few studies have been done on the specific reduction of cobalt in a superalloy (1-3). The principle reference to the overall role of cobalt in wrought superalloys is by Heslop (1) who reviewed the use

of cobalt in Nimonic alloys. Other studies on the role of cobalt have been limited to works on specific effects such as solid solution properties (4,5), gamma prime (1,6,7), carbides (1), creep and stress rupture (3,4), and phase stability (8).

MATERIALS AND EXPERIMENTAL PROCEDURE

The experimental compositions were designed with incremental substitution of nickel for cobalt on a weight % basis, Table I. Heats weighing 66Kg were vacuum induction melted and cast into two 7cm diameter molds. Sound portions of these ingots were homogenized at 1190°C (2175°F) for 24 hours and rolled at 1150°C (2100°F). Final roll passes at 1093°C (2000°F) produced 1.25cm thick rolldowns. This procedure produced duplex grain structures that were typically ASTM 2-4 with 20-30% ASTM 7. The series of heats with carbon from 0.020 to 0.030 had grain sizes of ASTM 7 with 30% ASTM 3-5.

Mechanical test specimens were prepared from longitudinal sections of rolldowns. Unless otherwise specified, test material was solution heat treated at 1010°C (1850°F) for 4 hours and oil quenched. Aging consisted of 847°C (1550°F) for 4 hours and 760°C (1400°F) for 16 hours with air cools from each temperature.

Table I. Chemical Compositions of Modified Waspaloy Heats*

Heat No.	(Weight %) *Balance Nickel							
	C	Cr	Co (Aim)**	Mo	Ti	Al	B	Zr
1650	.035	19.4	13.2(13.25)	4.05	3.07	1.35	.004	.06
1651	.031	19.4	12.4(12.5)	4.05	3.07	1.35	.004	.06
1652	.035	19.4	10.0(10.0)	4.02	3.05	1.32	.003	.06
1653	.036	19.3	8.1 (8.0)	3.99	3.01	1.33	.003	.06
1727	.033	18.9	5.8 (6.01)	3.92	2.94	1.34	.003	.06
1728	.038	19.5	3.6 (4.0)	3.96	3.02	1.36	<.001	.06
1729	.035	19.2	1.3 (2.0)	3.95	3.01	1.34	<.001	.06
1730	.040	19.5	0.01(0.0)	3.94	3.01	1.35	<.001	.06
1813	.027	19.7	13.1(13.25)	4.04	3.09	1.42	.003	.06
1816	.025	19.6	7.8 (8.0)	3.99	3.04	1.37	.002	.06
1817	.026	19.6	3.5 (4.0)	3.93	3.00	1.37	.001	.07
1818	.028	19.5	0.01(0.0)	3.90	3.02	1.37	.001	.06

**Apparent differences between analyzed cobalt and aim cobalt are due to inadequate standards at low levels.

Gamma prime solvus temperatures were determined using a Dupont 990 differential thermal analyzer with platinum crucibles and a scan rate of 20°C/min.

Extraction of gamma prime phase was done by electrolytic immersion in 1% citric acid and ammonium sulfate solution. Extraction of carbide phases was accomplished by electrolytic digestion in 10 vol. % hydrochloric acid in methanol. The same samples were then immersed in 10 vol. % bromine in methanol which dissolved all phases except MC carbides. Weight % $M_{23}C_6$, and dissolved carbon was then calculated from the remaining residues and carbon analysis.

High strain rate tensile data was obtained in a "Gleeble" with resistance heating.

RESULTS

Tensile ductility was unaffected and yield strengths and ultimate tensile strengths decreased only slightly at both room temperature and 538°C (1000°F) as cobalt decreased from 13.25 to 0.0 wt %. Room temperature yield strength decreased approximately 34 MN/m² (5 Ksi). These results are presented in Figures 1 and 2.

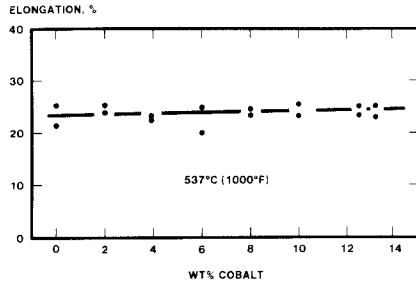
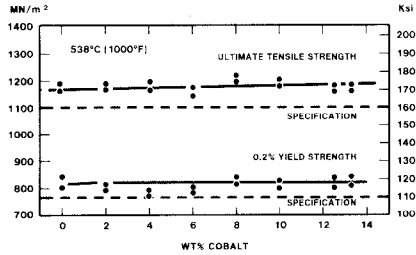
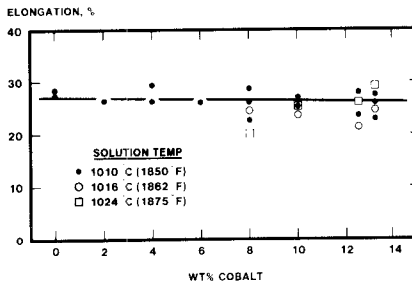
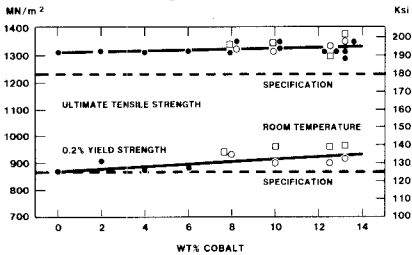


Figure 1. Room temperature tensile properties. Heat treatment modified with different solution temperatures.

Figure 2. Elevated temperature tensile properties.

Stress rupture lives at $732^{\circ}\text{C}/551\text{ MN/m}^2$ ($1350^{\circ}\text{F}/80\text{ Ksi}$) were reduced from approximately 70 hours at 13.25 wt% cobalt to 20 hours at 0.0 wt% cobalt for the high carbon heats. A reduction of stress rupture lives from 190 hours to 60 hours similarly occurred at 732°C when the stress was reduced to 482 MN/m^2 (70 Ksi). In both cases, no notch failures occurred and stress rupture ductilities were similar. At 816°C (1500°F), stress rupture lives again decreased with decreasing cobalt. This data is presented in Figures 3 and 4.

Creep curves shown in Figure 5 illustrate the sensitivity of creep rate to cobalt. At $732^{\circ}\text{C}/551\text{ MN/m}^2$ ($1350^{\circ}\text{F}/80\text{ Ksi}$), a six fold increase in the minimum creep rate is observed for no cobalt.

High strain rate (5 cm/sec) and medium strain rate (5 cm/min) hot workability data are presented in Figures 6 and 7. No variation in hot workability with cobalt was observed for the medium or high strain rate for specimens tested on heating. However, on-cooling ductility did appear to decrease with decreasing cobalt.

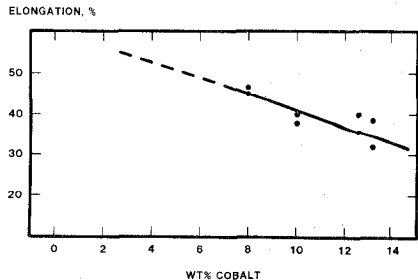
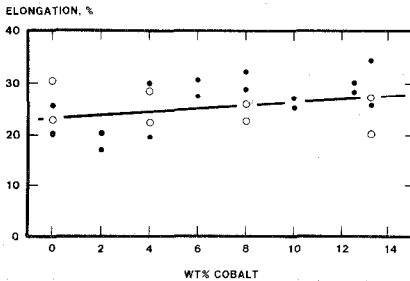
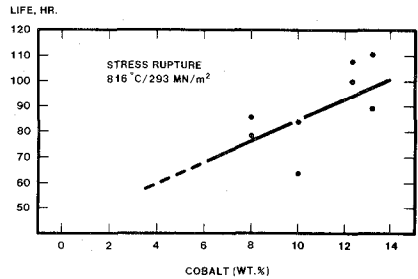
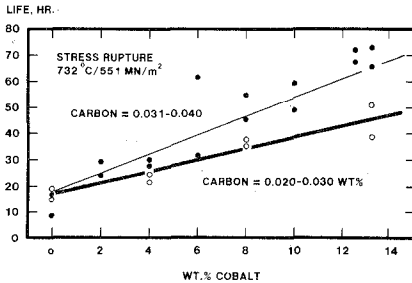


Figure 3. Stress rupture properties at $732^{\circ}\text{C}/551\text{ MN/m}^2$ ($1350^{\circ}\text{F}/80\text{ Ksi}$).

Figure 4. Stress rupture properties at $816^{\circ}\text{C}/293\text{ MN/m}^2$ ($1500^{\circ}\text{F}/42.5\text{ Ksi}$).

% ELONGATION

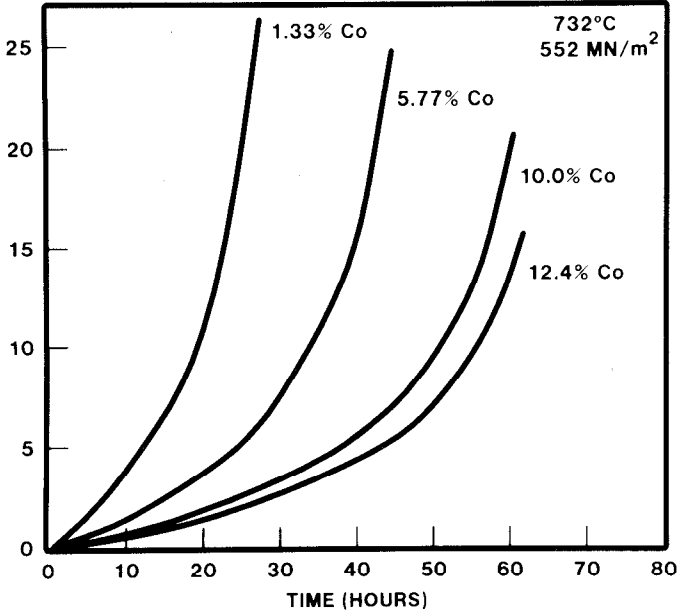


Figure 5. Creep curves at 732°C/552MN/m² (1350°F/80 Ksi).

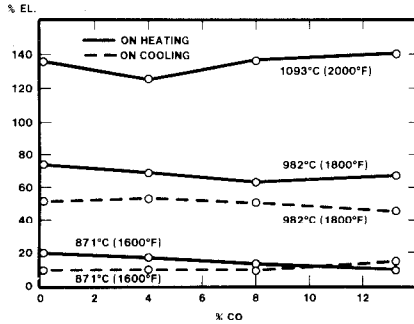
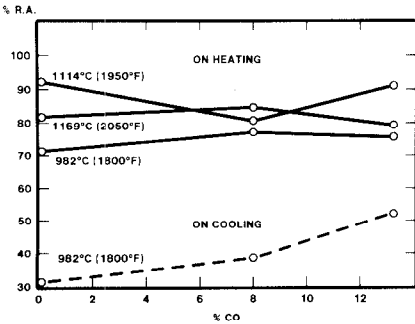


Figure 6. High strain rate workability results (13cm/sec); on cooling tests were heated to 1169°C(2050°F) for 5 min., then cooled to test temperature.

Figure 7. Hot tensile results (5 cm/min); on cooling tests were heat treated at 1169°C(2050°F) for 1 hours and fan cooled prior to tensile test.

Extraction data is presented in Figures 8 and 9. Reduced cobalt resulted in more MC ($Ti_{1.8}Mo_{2.2}C$) as rolled and increased amounts of $M_{23}C_6$ ($Cr_{21}Mo_2C_6$) at 843°C as presented in Figure 8. The weight % of gamma prime was found to decrease from 18 to 16% when cobalt was removed.

Energy dispersion spectrometry (EDS) of the extracted gamma prime residues is illustrated in Figure 10. Differences in the elemental partitioning appears to have occurred when cobalt was removed. While the differences are small, chromium and titanium appear to decrease while aluminum increases. Lattice spacing differences determined by x-ray diffractometers were small as illustrated in Table II.

Extraction results were supported by SEM of electro-polished and etched samples; Figure 11 illustrated the differences in gamma prime fraction and carbide precipitation.

The average gamma prime solvus temperatures did not change with decreasing cobalt. Values were within $\pm 3^\circ C$ of the control heat over the entire range of cobalt levels.

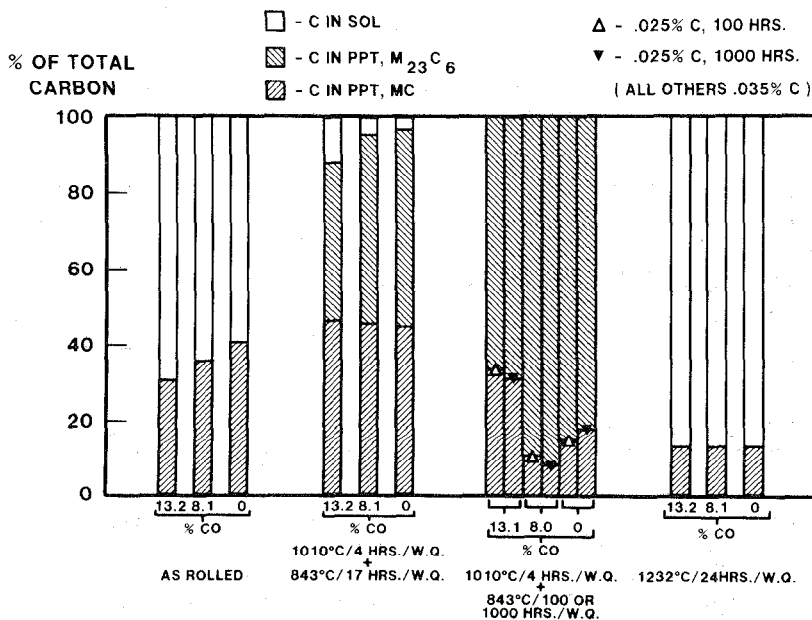


Figure 8. Carbon partitioning for three cobalt levels. Increase amounts of $M_{23}C_6$ are observed for lower cobalt heats. Different carbon levels are indicated.

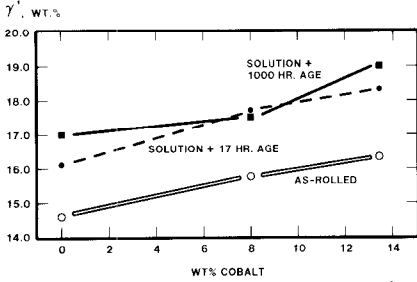


Figure 9. Weight % gamma prime as a function of cobalt and heat treatment.

Table II

Gamma Prime Lattice Parameters (A_{200})

Cobalt (Wt.%)	As-Rolled Condition	Solution + Age*
13.25	3.596	3.589
8.0	3.596	3.593
0.0	3.592	3.597

*1010°C- 4 hrs.-OQ
843°C-1000 hrs.-WQ

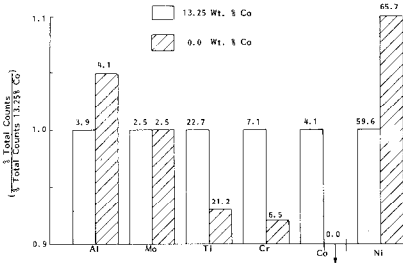


Figure 10. Changes in gamma prime partitioning with substitution of nickel for cobalt. Total counts represent XES peak heights. Gamma prime was extracted from material aged for 1000 hours at 843°C.

DISCUSSION

Interpretation of these results would have been greatly complicated if the gamma prime solvus temperature had been a function of cobalt. Since this was not the case, neither as-rolled nor heat treated grain structures were dependent on cobalt content. Also, relative atomic % did not vary since the atomic weights of nickel and cobalt differ by only 0.3%.

The decrease in creep resistance and stress rupture life could be related to various matrix and precipitate effects that have been correlated with creep strength in superalloys: gamma prime volume fraction, stacking fault energy, gamma prime antiphase boundaries, gamma prime morphology, gamma-gamma prime constraints, and carbides.

The observed reduction of gamma prime fraction certainly would result in reduced creep resistance. However, the difference in gamma prime fraction does not differ sufficiently to account for the full 50 hour drop in stress rupture life. Assuming that the observed 2% difference in weight % gamma prime corresponds to at least a 2% difference in volume fraction the data presented by Lubine (9)

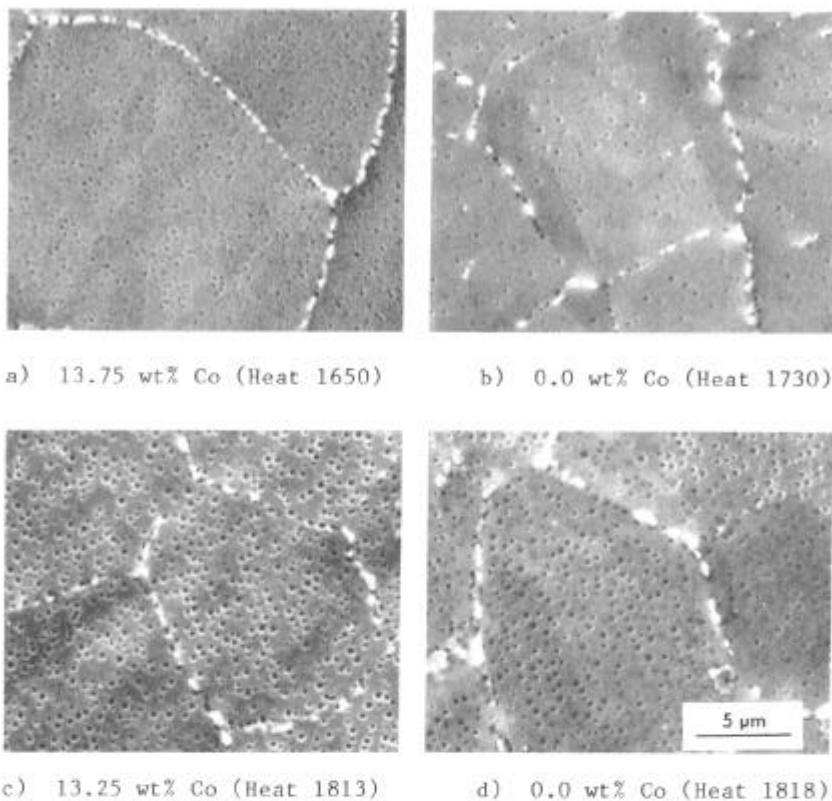


Figure 11. SEM micrographs of heat treated material: a & b) standard heat treatment, c & d) standard heat treatment + 1000 hours at 843°C (1550°F). (Magnifications are equal).

can be used to extrapolate a 10 hour reduction in a 100 hour rupture life. Similarly, using Larson Miller parameters and data presented by Decker (10), a 15 hour reduction in life is predicted. It can be concluded other factors affecting the matrix and precipitates must be considered.

Cobalt is a weak solid solution hardener in nickel since their atomic diameters differ by only 1%. Hazlet and Parker (4) showed that cobalt additions to pure nickel did not effect creep parameters. However, it has been documented that cobalt additions can strongly alter stacking fault energies. Heslop (1) reported that this may be the case for Nimonic 80A and 90 which are similar in composition to Waspaloy except that they do not contain molybdenum as shown below:

<u>Alloy</u>	<u>C</u>	<u>Cr</u>	<u>Co</u>	<u>Mo</u>	<u>Ti</u>	<u>Al</u>	<u>Ni</u>	<u>Other</u>
N-80A	0.08	20	--	--	2.4	1.4	Bal	--
N-90	0.08	20	17	--	2.4	1.4	Bal	--
Wasp	0.04	19.5	13.5	4.3	3.0	1.3	Bal	Zr, B

Beeston and France (5) estimated the contributions of various elements in Nimonic 80A and Nimonic 90 and showed that the % reduction in SFE from cobalt is half that of chromium and six times that of aluminum or titanium. These results indicate that indirect changes in SFE that would occur from changes in the partitioning of titanium, chromium, molybdenum or aluminum would be minor compared to the direct contribution of reduced cobalt.

Differences in carbide precipitation could also account for creep and stress rupture differences. The apparent increase in chromium carbide precipitation could lead to less discrete grain boundary precipitates and weakening of the adjacent matrix. The micrographs in Figure 11 exhibit coarser carbides for the lower cobalt alloys. TEM replication work is needed to identify changes in fine gamma prime precipitates near the grain boundary as was seen by Heslop (1).

Before significant reductions of any strategic element are made in superalloys, the feasibility of producing production quantities of modified chemistries must be considered. The hot workability results reported in Figures 6 and 7 are encouraging and no differences in hot workability were observed during rolling. However, a drop in ductility was observed for on-cooling testing at a high strain rate. Additional work is needed to further characterize this behavior. The lack of any changes in the gamma prime solvus temperature or the sensitivity to recrystallization (Figure 1) indicate that low cobalt modifications of Waspaloy could be fabricated without major changes in processing procedures.

The results of this study indicate that the contribution of cobalt may not justify its cost. The removal of cobalt in Waspaloy resulted in only minor tensile differences. Possibly creep resistance can be restored by increasing gamma prime formers such as Al and Ti or by increasing elements that are known to increase gamma prime precipitation such as chromium and iron (10). In either case, changes in carbon levels and carbide formers may have to be balanced. If these results are to be used for designing higher strength superalloys, care must be taken

to control changes in chromium partitioning which could result in phase instabilities.

CONCLUSIONS

1. Substitution of nickel for cobalt in Waspaloy results in the following:
 - . A slight decrease in yield and tensile strength with no change in tensile ductility.
 - . No change in gamma prime solvus temperature.
 - . Reduced stress rupture life and creep resistance.
 - . Slight decrease in gamma prime volume fraction.
 - . More MC as-rolled but more $M_{23}C_6$ with aging at 843°C (1550°F).
 - . No change in hot workability when tested on heating but an apparent decrease in ductility on cooling.
2. Increased creep rate and shorter stress rupture life in low cobalt Waspaloy appear to be partially due to lower gamma prime volume fraction. Other major contributors are higher stacking fault energies of the matrix and changes in carbide partitioning in grain boundaries.
3. Alloy modifications could result in the reduction or removal of cobalt from certain superalloys.

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