THE EFFECT OF TWO TRACE ELEMENTS ON CREEP RUPTURE PROPERTIES AND MICROSTRUCTURE IN A VACUUM MELTED COBALT BASE SUPERALLOY

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ABSTRACT

The influence of 90 ppm bismuth and 35 ppm selenium on creep rupture properties of a creep resistant cobalt base superalloy has been investigated. It is shown that this bismuth level causes a marked deterioration in rupture strength and ductility. The mechanical behavior in the bismuth containing heat was correlated with the microstructure and is discussed in terms of possible underlying controlling processes. The addition of selenium did not affect the rupture strength or rupture ductility.

INTRODUCTION

Laboratory investigations and service experience have demonstrated that several low melting and low solubility elements are harmful to strength and/or ductility of high temperature alloys, even when present in low concentrations. Metallurgical interest has been centered on the effects of bismuth, selenium, tellurium, and thallium in cast nickel base alloys[1,2]. In the literature[3,4] it has been pointed out that various impurities can have a significant influence on properties of other high temperature, high strength metallic systems. To date, little information has been reported on the effect of trace elements on mechanical properties in cobalt base superalloys, or at least none has been identified and documented. This investigation reports the effects of one concentration each of bismuth and selenium on creep rupture properties and on the microstructure of a high strength cobalt base superalloy.

EXPERIMENTAL PROCEDURE

MATERIAL

Bismuth and selenium was added individually at one concentration to two 15 lb. ingots of a virgin heat of a cobalt base alloy containing 0.6% C, 23.4% Cr, 10.4% Ni, 7% W, 3.7% Ta, .17% Ti and .14% Al. The aim was to add 100 ppm Bi or 100 ppm Se respectively. The Bi or Se additions were prepared by blending the contaminants with high purity nickel powder (50 grams) followed by compacting to a pellet. The amount of trace elements added to the nickel powder was based on an 80% recovery.

Oversize test bars were cast under identical conditions with a metal superheat of 275°F and a mold preheat of 1800°F. The first group of specimens, the control group, was cast from a virgin heat. Trace metal additions were made in the melting cycle by back filling the melt chamber with argon and placing the pellet into the melting crucible followed by re-evacuating and bringing the charge back to pouring temperature. All castings were in the form of test specimens 3.50 inches long by 0.280 inches in diameter cast into a single mold.

The concentrations of Bi and Se were determined by utilizing the highly sensitive non-flame atomic absorption spectrophotometry. The analysis yielded 35 ppm selenium and 90 ppm bismuth recovered in the two heats.

CREEP RUPTURE TESTS

Creep specimens were tested in the as cast condition at 1650°F and 1800°F at various stress levels for periods of time from 20 hrs. to 3000 hrs. The two temperatures were chosen to be representative of the operating range of a stator blade in a gas turbine.

Test specimens were machined from the oversized test bars. The gauge diameter was 0.250 inches and the gauge length was 1.250 inches. All tests were conducted in air in standard lever arm creep frames.

RESULTS

CREEP RUPTURE STRENGTH AND DUCTILITY

Results of the creep rupture tests are summarized in Table I.

Table I

Creep Rupture Test Data

Specimen Identity	Test Temp. °F	Initial Stress ksi	Rupture Time H	Min. Creep Rate %/H	Red. of Area %
JE09, Control	1800	16	95.8	3.8×10^{-2}	20.9
JE09, Control	1800	16	119.1	1.1×10^{-2}	7.2
JE09, Se	1800	16	75.8	5.8×10^{-2}	25.8
JE09, Se	1800	16	80.7	3.9×10^{-2}	23.5
JE09, Bi	1800	16	75.1	2.2×10^{-2}	8.9
JE09, Bi	1800	16	77.3	2.5×10^{-2}	9.5
JE09, Control	1800	10	3041.5	1.4×10^{-4}	2.0
JE09, Se	1800	10	1745.7	1.5×10^{-4}	2.5
JE09, Bi	1800	10	904.1	4.9×10^{-4}	3.1
JE09, Control	1650	27	76.1	4.9×10^{-2}	19.7
JE09, Se	1650	27	23.6	3.9×10^{-1}	27.0
JE09, Bi	1650	27	31.0	6.9×10^{-2}	4.8
JE09, Control	1650	18	1753.2	8.7×10^{-4}	13.8
JE09, Se	1650	18	1595.8	1.5×10^{-3}	15.3
JE09, Bi	1650	18	1141.2	4.3×10^{-4}	5.5

The data indicate a pronounced difference in rupture strength between the impure heats and the control heat at longer times and at the higher test temperature. At the lower test temperature the results show the absence of appreciable effects on rupture strength due to impurities.

The effect of impurity additions on creep strength can be made by comparing the variation of minimum creep rate for each stress. The data indicate that minimum creep rates for the impure heats are only slightly higher than for the control composition. A stepwise regression analysis yielded the following equations:

$$\text{Log } \varepsilon_s' \text{ control} = 22.984 - \frac{66986}{\text{Tin } °R} + 0.302 \times \text{stress in ksi}$$

$$\text{Log } \varepsilon_s' \text{ bismuth} = 23.083 - \frac{66986}{\text{Tin } °R} + 0.302 \times \text{stress in ksi}$$

$$\text{Log } \varepsilon_s' \text{ selenium} = 23.184 - \frac{66986}{\text{Tin } °R} + 0.302 \times \text{stress in ksi}$$

The variation of reduction in area at rupture between the three groups, tabulated in Table I, shows for each heat high ductility values at short rupture lives followed by a decrease in ductility with further increase in time to rupture. While a magnitude difference in ductility exists at the short time between the Bi heat and the control or Se heat, it appears the effect of impurities tend to become negligible at longer times for the values of all heats converge for times to rupture of about 10^3 hours.

MICROSTRUCTURE ASPECTS

A microstructural study was performed with a view to identify the structural features occurring during creep. The grain size of the control and bismuth containing heats was similar whereas the grain size in the selenium containing heat was finer and more columnar. The mean values of the secondary dendrite arm spacings were similar for all heats (35 μm) with the variation being slightly larger for the heat contaminated with bismuth.

The as cast microstructure of this alloy has been determined previously[5]. In an attempt to monitor the structural changes that occur during creep the various carbide phases were carefully examined. It was observed that the large script-like MC carbides were stable during creep, Fig. 1. However, copious amounts of fine $M_{23}C_6$ and MC carbides precipitated within the dendrite areas. Also note in Fig. 1 that there is a greater amount of fine precipitates in the bismuth heat than in either the control or selenium heat. It was also observed that MC or $M_{23}C_6$ carbide particles precipitated preferentially within the dendrite areas of the bismuth heat specimens during creep.

To determine the extent of decomposition and total amount of carbide precipitated during creep, the matrix was dissolved electrolytically and the insoluble residue was collected, weighed and identified by X-ray diffraction[6]. Table II summarizes the variation in the type and amount of carbides found in these heats before and after creep rupture test.

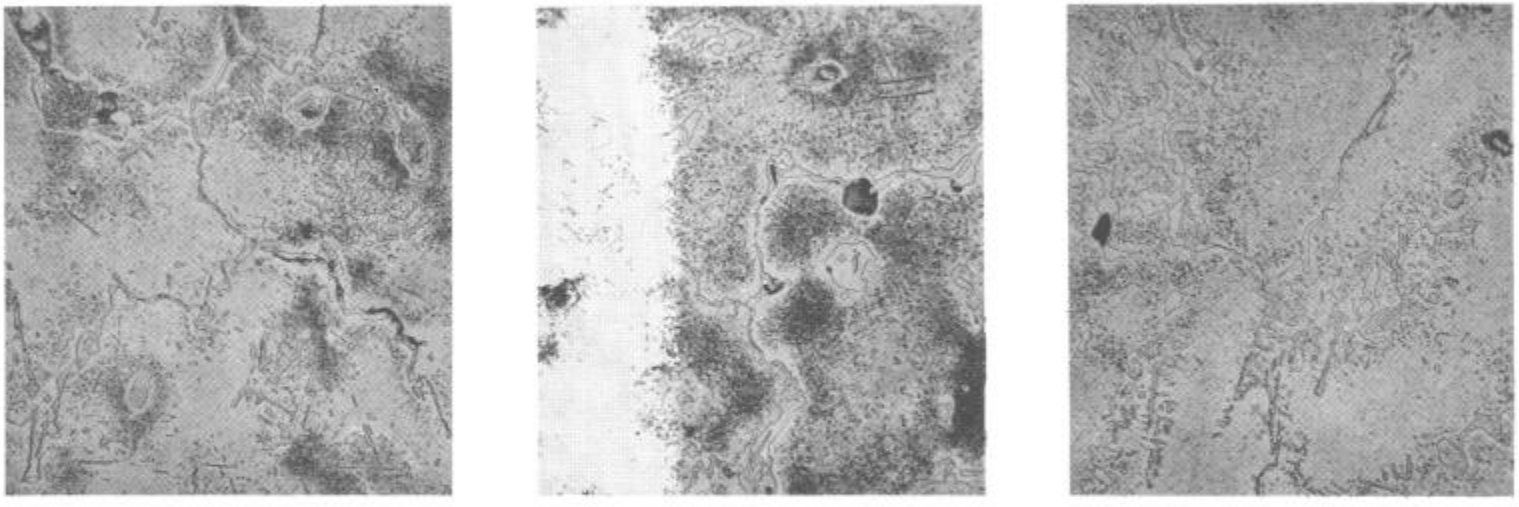
Table II

Variation in the Type and Amount of Carbides
Before and After Creep Rupture Test

	AS CAST			AFTER CREEP RUPTURE TEST*			
	TOTAL	EST RELATIVE AMT.		TOTAL	EST. RELATIVE AMT.		
SAMPLE	CARBIDE (WT. %)	MC (WT. %)	M_7C_3 (WT. %)	CARBIDE (WT. %)	MC (WT. %)	M_7C_3 (WT. %)	$M_{23}C_6$ (WT. %)
JE09, Control	7.2	5.4 (4.415)**	1.8	10	6 (4.417)**	-	4
JE09, Bi	5.1	3.8 (4.415)**	1.3	9	6.3 (4.417)**	.9	1.8
JE09, Se	7.0	5.3 (4.403)**	1.7	8.5	4.8 (4.406)**	.4	1.3

*Threaded area of 1650°F/27 ksi sample
**Lattice Parameter

The as cast microstructure of the three heats consists of MC and M_7C_3 carbide phases of about the same relative ratio. Specific composition of these carbides depends upon the rate of cooling. The observed difference in lattice parameter of the MC carbide phase indicates the selenium heat solidified differently than the other two. During creep the metastable M_7C_3 phase decomposes into $M_{23}C_6$ and MC carbides, and in addition they can also precipitate from the matrix. The total amount of carbide residue increases as a result of the creep rupture test. Table II shows that there is a greater increase in total carbide precipitated during creep in the bismuth heat than the control which, in turn, is greater than the selenium heat.



(a)
Control Heat

(b)
Bi Containing Heat

(c)
Se Containing Heat

FIG. 1 - MICROSTRUCTURE OF A COBALT BASE SUPERALLOY WITH DIFFERENT TRACE METAL ADDITIONS

METALLOGRAPHY OF CRACKS

Longitudinal and transverse cross sections of the various stress rupture tested specimens were prepared and examined. All failures were intergranular. In all cases cracks were present along the periphery of the gage section but the extent of the cracks varied depending upon the impurity added. Examination of the bismuth heat showed the length of these cracks was more extensive when compared to those of the control heat. A larger number of shallow cracks were found in the Se containing specimens. The larger number of cracks were attributed to the finer grain size. A large number of interconnected networks of r-type voids were found in the interior of the Se heat specimens. Examination of specimens from the other heats indicated they also contain these voids but the number decreased sharply from control to Bi heat respectively. In all cases, voids or void networks were present only on boundaries oriented transverse to the stress axis.

AUGER ANALYSIS

To examine the possibility of grain boundary segregation of Bi or Se, specimens from these heats were fractured at 75°F in the vacuum chamber of a Scanning Auger Microprobe (SAM). The bismuth concentration was analyzed at several different areas on the surface using a focused electron beam (5-10 μm in dia.). The concentration of bismuth in the bulk of the sample away from the grain boundaries was determined by sputtering the fracture surface with argon ions. Several selenium samples were fractured in the SAM, however, fracture occurred mainly interdendritic where no selenium was found.

Well defined peaks are observed for bismuth at the fracture surface clearly indicating segregation of bismuth at the grain boundary. From the peak heights the concentration of bismuth was estimated based on knowledge of the relative sensitivity factors and using the procedure described in Ref. 7. The estimated concentration of bismuth was found to be 11 W/o or 2.5 a/o.

DISCUSSION

The present study has shown that marked differences in rupture strength and ductility exist between the bismuth containing heat and the control heat, but the effect of selenium on rupture properties is less pronounced. As described previously, the differences in rupture strength between the bismuth heat and the control heat exist only at longer rupture times and higher testing temperature. Significant changes in the creep ductility (as measured by the reduction in area at rupture) were observed at shorter times at both test temperatures. Examination of the microstructure of the two heats did not reveal variations in dendrite arm spacing, grain size, carbide phases, and their morphology. The only detectable distinction between the two heats was the segregation of bismuth to the grain boundaries.

The mechanisms by which impurity species affect creep properties, in particular rupture ductility, include the strengthening of the matrix which has the effect of concentrating deformation near grain boundaries during creep, and/or segregation of impurities to grain boundaries resulting in a net lowering of the fracture surface energy at grain boundaries. In the present case, the results indicate that both mechanisms are operative, but not at all temperatures and stresses. For example, at higher stresses and lower temperature, both may be operative; whereas at lower stresses and higher temperature, only weakening at the grain boundaries is important as described below.

The general pattern of variation of % reduction in area at rupture with rupture life is consistent with the results of many other investigators, namely, that the ductility decreases with increasing rupture life. In steels it has been shown that the decrease in ductility is due to a shift in deformation from grains to the grain boundaries [8,9], where the fracture changes from crystalline to an inter-crystalline mode. In creep resistant superalloys the fracture mode is normally found to be inter-crystalline although at higher stresses, deformation can occur in the matrix as well as near grain boundary areas. The high ductility observed in the control heat at higher stresses is believed to be a direct result of the above factor.

The effect of bismuth at higher stresses results in an increased amount of carbides precipitating within dendrite areas (matrix). As a result, grain deformation becomes increasingly more difficult and the secondary creep stage extends to much longer times than the control specimen. Eventually, a crack is formed but it propagates rapidly due to the lowering of the effective surface energy at the grain boundaries caused by the segregation of bismuth. On the other hand, tertiary creep starts sooner for the control heat because cavities form, grow and coalesce due to the softer matrix and grain boundary sliding. The rate of cavity formation and growth is slow which results in longer tertiary stage of creep than that exhibited by the bismuth heat. The net effect of the above is the rupture life of the bismuth heat is similar to the control (which could be fortuitous), but the rupture ductility is significantly lower.

At lower stresses grain deformation becomes increasingly more difficult because of the high shear strength of the matrix due to carbide precipitation. Consequently, creep deformation will occur almost entirely by grain boundary sliding which will lead to inter-crystalline failure with low total ductility. The above mechanism can explain the low ductility at rupture for specimens tested at 1800°F and 10 ksi. Furthermore, due to the net lowering of the fracture surface energy at grain boundaries by bismuth segregation, tertiary creep occurs at shorter times for this heat and rupture occurs prematurely. This weakening of the grain boundaries increased the crack growth rate significantly which is consistent with the fracture mode observed. That is, the number of secondary cracks are fewer and the length of these cracks is more extensive for the bismuth heat compared to the control heat.

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