THE EFFECT OF SMALL AMOUNTS OF LEAD ON THE CREEP PERFORMANCE OF A CAST Ni-Cr-BASE ALLOY

G B Thomas
T B Gibbons
Division of Materials Applications, National Physical Laboratory, Teddington, Middx, U K

Study of the effects of trace amounts of Pb on the creep and stress-rupture properties of Mar M002 indicated that 2ppm Pb would reduce creep performance at 850°C. Optical metallography showed that the deleterious effect of Pb was associated with greatly increased development of intergranular cavitation and cracking during testing at high temperature. Auger electron spectroscopy established that Pb segregated to the cavitated grain boundaries.

INTRODUCTION

Trace amounts of certain elements can have a very significant effect on the properties of Ni-Cr-base alloys for service at high temperatures and control of these elements is essential for optimum creep performance.

The recent review (1976) by Holt & Wallace (1) provided a comprehensive survey of the influence of both beneficial and deleterious trace elements in Ni-base superalloys. They concluded that it was not possible to specify compositional limits for deleterious impurities which could be applied to all Ni-base alloys. This is because synergistic effects may exist between different trace elements or between impurities and alloying elements. Furthermore, the work of Lund (2) on Mar M200 showed that the magnitude of both harmful and beneficial effects was influenced by the temperature of test.

The deleterious effects of trace elements on creep performance are invariably associated with grain boundary embrittlement but until recently there has been little detailed information on the mechanism involved. It has usually been assumed that segregation of the impurity to the grain boundaries occurred, as was shown for Cu embrittled by Sb (3). The present authors (4) established that while ppm levels of Pb and Te seriously reduced the stress-rupture properties of Nimonic 105 at 815°C, similar amounts of Tl and Se had only a small effect. Pb and Te caused greatly increased cavitation during creep and Auger electron spectroscopy (Aes) confirmed that the impurity had segregated strongly to the cavitated interfaces. Recent work (5) on type 304 steel provides, incidentally, additional support for the view that impurities, in this case S, segregate to cavitated interfaces in wrought alloys. Less direct mechanisms can also be important and in certain bainitic steels tramp elements enhanced the intergranular precipitation of non-coherent MnS particles resulting in increased cavitation and reduced ductility in creep (6).

There is some evidence that the influence of impurities is greater in cast than wrought alloys and the creep performance of an unidentified cast superalloy has been shown to be highly sensitive to the presence of Bi (7). Recent studies using Aes have shown that (i) Bi, Te and Pb segregate to grain boundaries in B1900 and Mar M200 during fracture at 870°C (8) and (ii) the reduction in hot ductility of cast superalloys was associated with intergranular segregation of S (9). However the amount of information available on cast alloys is not extensive and consequently a detailed investigation has been carried out of the effect of trace amounts of Pb on the creep and stress-rupture properties of the cast alloy Mar M002. This paper describes the results obtained. The work was undertaken in close collaboration with Rolls-Royce Ltd who assisted in planning the experimental programme, advised on relevant test conditions and supplied the materials.

EXPERIMENTAL

Materials and Mechanical Testing

The materials consisted of cast sticks of a base alloy with no added impurity and of a series of Pb-contaminated alloys. Details of the compositions are given in Table 1. The cast sticks were aged at 870°C for 16h and air-cooled. The average grain size was ~0.6mm.

Table 1. Compositions of Mar M002 Alloys, wt%

Cr	W	Co	Al	Ti	Ta	Hf
9.01-9.06	10.0	9.95-9.97	5.72-5.74	1.50-1.52	2.50-2.54	1.58-1.72

Zr	B	C	S	Ni	Pb (ppm)
.060-.063	typically .013	typically 0.15	typically 0.004	BAL	<0.1,5,20,23 & 100

Plain and notched (to BS 3500,Part 1) specimens having the same net gauge diameter of 4.5mm (0.177 in) were used for stress-rupture tests at 850°C and 465 Nmm^{-2} (30 tonf in^{-2}). Creep tests were carried out at 850°C and 350 Nmm^{-2} (22.7 tonf in^{-2}) using specimens with a gauge diameter of 6.3mm (0.25 in).

Metallography and Creep Damage Studies

Fractured specimens and specimens from interrupted tests were slit longitudinally and prepared for examination in the optical microscope. The final stage of preparation consisted of a repeated process of polishing with gamma alumina and etching in 10% HCl - ethanol at 6V until a good surface allowing unambiguous identification of intergranular cracks and cavities was obtained.

Creep damage was assessed optically by scanning the section at a magnification of X500 and measuring the lengths of cracks and cavities projected normal to the specimen axis. The total of these projected lengths was then expressed as a proportion of the total projected lengths of all the grain boundaries encountered during the scan.

Microporosity, which was generally at a low level and fairly uniformly distributed in all the specimens, was usually readily identified by the characteristic shapes. However, in the case of a few very small voids (<2μm dia) a positive distinction between pores and cavities was not possible. These were included with the creep damage and a small correction, averaging about 0.15%, was subsequently made using a "background" figure for such voids determined from the unstressed heads of the specimens.

Auger Electron Spectroscopy

A stress-rupture test on a plain specimen containing

100ppm Pb was stopped prior to fracture after the elapse of about 30% of the expected life to rupture, ie 2h. The parallel length was reduced to ~1mm diameter by grinding and the specimen was then fractured at room temperature under vacuum inside the Auger equipment. One half of the specimen was examined by a low power Auger scanning microscope having an ultimate resolution of 50μm and subsequently scanning electron microscopy was used to study the appearance of the fracture surface.

RESULTS

Stress-Rupture and Creep Tests

Fig.1 shows the deleterious effect of Pb on life to rupture of both types of specimen and on reduction of area in the plain specimens. The reduction of area in notched specimens of the base alloy was small and was therefore only slightly affected by the presence of Pb. Fig.1c shows the average stress-rupture properties after normalising with respect to those of the base composition. Evidently the sensitivity of notched specimens of Mar M002 to the presence of Pb was not significantly greater than that of plain specimens. This is in contrast to the behaviour of Nimonic 105 although both alloys were notch-strengthened (4).

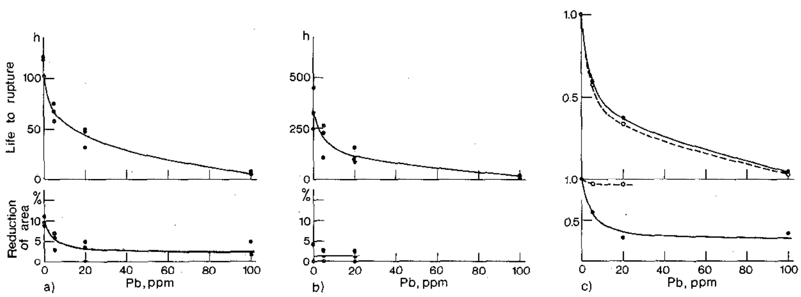

Fig.1. Effect of Pb on stress-rupture properties of Mar M002. a) Plain specimens b) Notched specimens c) Normalised average:- —o— plain specimens --o-- notched specimens

The results in Table 2, show that Pb had no significant effect on minimum creep rate. The reduced life to rupture was therefore a consequence of the decreased ductility, consistent

Table 2. Results of Creep Tests at 850°C and 350 Nmm^{-2} and Measurements of Intergranular Damage

Alloy	Duration h	Elongation %	Minimum creep rate $10^{-5}h^{-1}$	Creep damage %
base alloy	496	2.5	2.5	2.4
	311*	1.5	3.7	0.6
base alloy	122	0.5	3.4	19.7
with 23ppm Pb	40*	0.2	3.9	1.0

* Stopped before fracture

with the results of the stress-rupture tests and with previous experience (4).

Metallography and Creep Damage Characteristics

Optical microscopy of sections from fractured test pieces revealed a heterogeneous, dendritic structure with highly convoluted grain boundaries. In addition to the large volume fraction of relatively coarse particles of γ' there was a high proportion of eutectic γ-γ' both within the grains and at the grain boundaries, and much of the length of the boundaries was in contact on one or both sides with such eutectic regions. Typical blocky and script-type MC carbides were observed within the grains and fine platelets of carbide, presumably $M_{23}C_6$, were present at the grain boundaries. There were no apparent differences between the microstructures of the base alloy and those containing Pb either before or after testing.

Failure in the stress-rupture and creep specimens was predominantly intergranular and longitudinal sections revealed cracked grain boundaries remote from the fracture. In the base alloy some of the intergranular cracks originated at the specimen surface and were oxidised whereas others were entirely internal showing no signs of oxidation. In contrast, the alloys containing Pb showed very few cracks originating at the surface but many more internal boundaries were cracked. This was particularly evident in the creep specimens, which were tested at a lower stress and, in these, intergranular cavities could also be resolved, Fig.2. There was a tendency for the intergranular damage in the base alloy to be greater adjacent to the fracture where the local strain was presumably larger. In the Pb-contaminated alloy there was a more even distribution of damage along the specimen gauge length, Fig.3.

In Fig.4a creep damage is plotted as a function of time of test and compared with the creep curves. When 23ppm Pb was present damage occurred early, after about 10% of creep life, but in the base alloy significant damage was only observed in tertiary creep after more than half the expected life. Also, Fig.4b shows that creep damage increased rapidly with strain in the alloy containing Pb and in the fractured specimen the average amount of damage was about ten times greater compared with the base alloy.

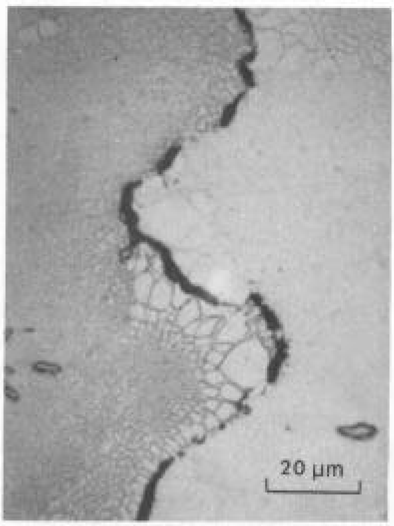

Fig.2 Cavitation and cracking at grain boundaries in Mar M002 containing 23ppm Pb after creep testing; stress-axis horizontal.

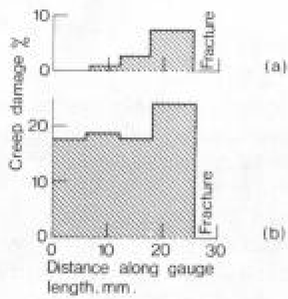

Fig.3 Effect of Pb on the distribution of damage in fractured specimens of Mar M002 a) base alloy b) alloy with 23ppm Pb.

Auger Electron Spectroscopy

The Augergraph of Fig.5a shows the distribution of Pb on the fracture surface of the partly stress-rupture tested specimen. The average level of surface contamination was about 0.1 monolayer but the peak value was estimated at about 1 monolayer. Ion sputtering confirmed that the Pb was present as a surface layer. The scanning electron micrograph (Fig.5b) of part of the area of maximum contamination shows evidence of intergranular cavitation, confirming that the segregation of Pb was associated with the cavities formed during creep.

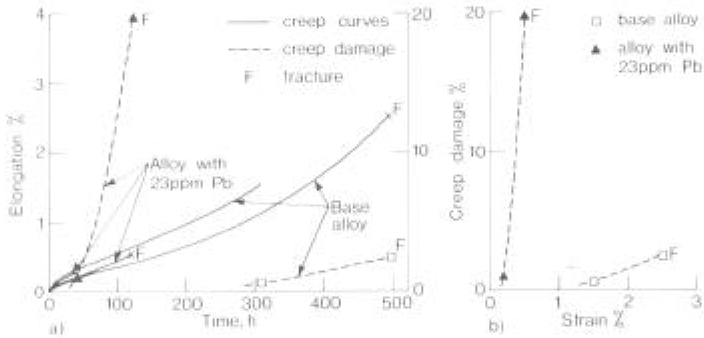

Fig.4. Effect of Pb on creep behaviour and damage accumulation in Mar M002.

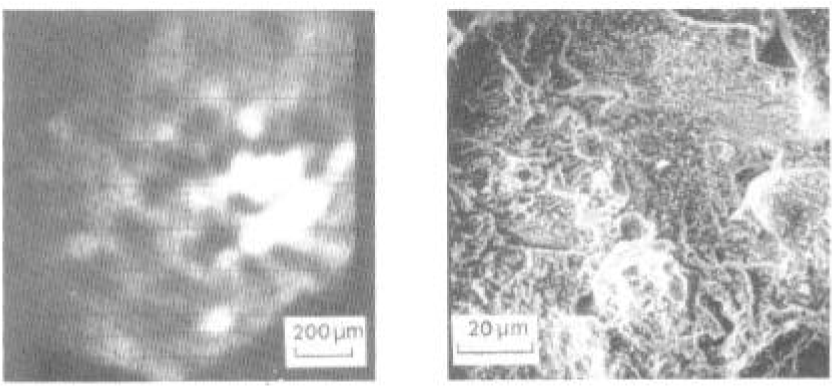

Fig.5. a) Augergraph showing distribution of Pb on the fracture surface of the partly stress-rupture tested specimen of Mar M002 b) Scanning electron micrograph of the area of maximum contamination.

DISCUSSION

The results of the stress-rupture tests suggest that a significant decrease in life to rupture and in ductility of Mar M002 would occur at concentrations of Pb as low as 1 or 2 ppm. The reduction in creep performance was associated with the greatly increased susceptibility to intergranular cavitation and cracking when Pb was present. This evidence, along with that obtained with Aes confirming the segregation of Pb to a cavitated region of the fracture surface, is consistent with the results of earlier work (4).

Thus the circumstantial evidence suggests that the embrittling effect of Pb in Mar M002 was controlled by a mechanism similar to that proposed for Nimonic 105, viz that segregation of the impurity reduced the surface energy, γ_S, and consequently increased the amount of cavitation during creep by stabilising cavities of smaller radius, r, since

$$r = \frac{2\,\gamma_S}{\sigma} \qquad \ldots.(1)$$

where σ is the applied stress.

Comparison with the previous work indicates that at concentrations of less than 30ppm the effect of Pb in reducing life to rupture was greater in the cast alloy, which would be expected to be more sensitive to segregation given the large grain size and heterogeneous nature of the microstructure.

An interesting feature of the development of intergranular damage in the creep specimens was that, in common with the internally developed cracks, the extent of surface cracking increased with strain but its rate of development was not enhanced by the presence of Pb, in contrast to that of internal cracks. This appears to indicate that the grain boundaries that intersect the surface are less sensitive to the embrittling effect of Pb, perhaps because Pb in the vicinity diffuses preferentially to the free surface rather than to grain boundary sites. Alternatively, local changes in composition close to the surface as a result of oxidation or preferential diffusion of particular alloying elements may inhibit the embrittling potential.

CONCLUSIONS

1) Lead seriously reduced the life to rupture and ductility of Mar M002 at 850°C and a level of more than 2ppm would be expected to impair the creep performance.

2) The presence of Pb in Mar M002 was associated with the appearance of intergranular damage at a much earlier stage of creep life and with considerably more rapid development of cracking with increasing strain compared with uncontaminated material.

3) Lead segregated to the cavitated intergranular surfaces of a stress-rupture tested specimen of Mar M002 containing a concentration of 100ppm Pb.

4) The use of notched rather than plain test pieces in stress-rupture tests did not give a significantly more sensitive indication of the presence of harmful amounts of Pb in Mar M002, in contrast to previous experience with Nimonic 105.

5) At low concentrations of impurity the cast alloy Mar M002 showed a greater sensitivity to the presence of Pb than the wrought alloy Nimonic 105.

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REFERENCES

(1) R. T. Holt & W. Wallace, Int.Met.Rev.,Vol 21, 1976, p.1.

(2) C. H. Lund: unpublished work reported in "The Superalloys" (ed.C.T.Sims & W.C.Hagel), New York, Wiley, 1972, p.567.

(3) H. R. Tipler and D. McLean, Met.Sci.J., Vol.4,1970,p.103.

(4) G. B. Thomas and T. B. Gibbons, Metals Technology, Vol.6, No.3, 1979, p.95.

(5) J. Y. Park, S. Danyluk and D. E. Busch, "Weldments-Physical Metallurgy and Failure", Bolton Landing Conference, Aug.1978.

(6) C. J. Middleton, Central Electricity Research Laboratories Report No.RD/L/R 1995, 1979.

(7) R. A. Cremisio and D. A. Shinn, Proceedings of the Fourth International Symposium on Electroslag Remelting, Tokyo, June 1973.

(8) J. M. Walsh and N. P. Anderson, "Superalloys: metallurgy and manufacture, Seven Springs Pensylvania 1976" (ed. B. H. Kear, D. R. Muzyka, J. K. Tien and S. T. Wlodek), Baton Rouge, Claitors, 1976, p.127.

(9) S. Yamaguchi, H. Kobayashi, T. Matsumiya and S. Hayami, Metals Technology, Vol.6, No.5, 1979, p.170.