

THE ROLE OF SMALL AMOUNTS OF MAGNESIUM IN NICKEL-BASE AND
IRON-NICKEL-BASE SUPERALLOYS AFTER HIGH TEMPERATURE LONG TIME EXPOSURES

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The role of Mg after 650°C/5000hrs and 850°C/1200hrs long time exposures was studied in GH169 and GH220+ respectively. A small amount of Mg can prolong the secondary and tertiary stages of creep, thus resulting in increases of stress rupture life and ductility for 1.5-2.5 and 2-3 times respectively. The optimum content of Mg will be moved to lower level by the high temperature long time exposure. Magnesium behaviour in both alloys has been illustrated as equilibrium segregation to grain boundaries by AES, IMA and thin foil TEM analyses. The segregation rate of Mg has been demonstrated to be very slow. Magnesium can also refine grain boundary carbide M_6C and depress grain boundary cellular precipitation of $\delta-Ni_3Nb$ in GH220 and GH169 respectively. These beneficial effects of Mg can be retained after high temperature long time exposure.

Introduction

Recent increases in price of Co and limitation in Co supply provided incentive for reduction and elimination of Co in nickel-base superalloys. A number of investigations on the role of Co in superalloys have been published (1-5). One of the important effects of Co, in general, is that Co can intensively increase stress rupture life and decrease secondary creep rate. It brings about the main difficulty for elimination of Co in nickel-base superalloys. It is early recognized that a small amount of minor elements such as B, Mg, Ca and rare earths etc. can also improve the stress rupture and creep properties significantly. Therefore, an intention can be made as a general way to reduce Co content in superalloys, that the stress rupture and creep strength drops due to remove Co from alloy can be hopefully balanced by superimposed addition of minor elements. We considered that Mg should be a suitable element. The beneficial effect of Mg has been confirmed since 1960's (6-13). However, it is dubious that the effect can be

+ GH169 and GH220 are high performance superalloys of Chinese National Specification. GH169 is similar to American superalloy Inconel 718.

retained after long time exposure at high temperature up to 850°C and higher. The systematic studies must be undertaken to understand this important practical and theoretical problem.

The Mg behaviour in superalloys is also not fully understood. Topilin (8) suggested Mg to be a surface active element, but any direct experimental evidence has not been obtained. Chernjak (9) showed that Mg can combine with S and therefore depress the deleterious effect of this impurity. Some publications (8,10) indicated that Mg can change the morphology of grain boundary carbides. The purpose of the present paper is to demonstrate the role of Mg on creep behaviour and microstructure in superalloys after high temperature long time exposures, and to discuss the possibility of using Mg in a general way to balance the creep strength loss due to reduction of Co content in superalloys.

Materials and Procedures

Typical disc alloy GH169 and blade alloy GH220 both with various Mg contents were selected for this investigation. Chemical compositions of experimental alloys are shown in Table I. Both alloys were vacuum melted and hot rolled out in bars. The heat treatments were conducted as following: GH169-950°C/1hr/A.C.+720°C/8hrs/F.C. to 620°C/8hrs/A.C.; GH220-1220°C/4hrs/A.C.+1050°C/4hrs/A.C.+950°C/2hrs/A.C. long time exposure treatments were performed at 650°C up to 5000 hrs for GH169 and at 850°C up to 1200 hrs for GH220.

Table I. Chemical compositions of experimental alloys (Wt %)

Alloy	C	Cr	W	Mo	Al	Ti	V	Co		
GH169	0.027	19.50	-	3.14	0.44	1.03	-	< 0.10		
GH220	0.046	9.90	5.35	5.40	4.12	2.30	0.27	14.55		
Alloy	Nb	Mn	Si	S	P	B	Fe	Ni	Mg	
GH169	5.05	<0.10	0.070	0.005	0.007	0.0053	Bal.	52.50	0.0001 0.0094	
GH220	-	0.02	0.060	0.007	0.004	0.013	-	Bal.	0.0008- 0.0190	

Grain boundary segregation of Mg was analysed by AES and IMA (ion microprobe analysis). Specimens were impacted at liquid nitrogen temperature for getting intergranular fracture, then immediately put into vacuum chamber. This procedure could avoid any contamination except surface gas absorption. The perpendicular sputtering rate was 1Å/sec and 0.5-5Å/sec for AES and IMA respectively. The distribution of Mg on the grain boundaries was analyzed by X-ray microanalysis directly on thin foil in TEM with microprobe (about 20Å width (14)).

Experimental Results

The influence of Mg on mechanical properties of GH220

The influence of Mg on 950°C tensile properties of GH220 before and after 1200hrs exposure at 850°C is shown in Fig.1. Tensile ductility at 950°C can be doubled at almost same ultimate strength level by Mg addition. This beneficial effect still keeps in function after long time exposure.

Fig.2 shows the influence of Mg on 940°C/216MPa stress rupture properties, appropriate addition of Mg can even triple stress rupture life and ductility. It is clear from Fig.2, there existed an optimum Mg addition in

alloy GH220. Any under or over-addition of Mg in the alloy both can not meet the best stress rupture properties. The beneficial effect of Mg addition on stress rupture properties is also kept in function after long time exposure at 850°C, but the optimum content of Mg is moved to lower level.

Fig.3 shows that the experimental alloys with more than 0.005%Mg possess good stress rupture properties under normal heat treated condition, but the stress rupture life is gradually decreased during exposure. Finally after 1200 hrs exposure at 850°C, the stress rupture lives of those alloys are already shorter than that of alloy with 0.005% Mg, but is still longer than that of Mg free alloy.

Typical creep curves (850°C/343MPa) of GH220 with various Mg contents, under normal heat treated condition and after 850°C 1200 hrs exposure, are shown in Fig 4. It indicates that Mg addition almost has no influence on steady-state creep rate (10-20×10⁻³hr⁻¹), but Mg can substantially prolong

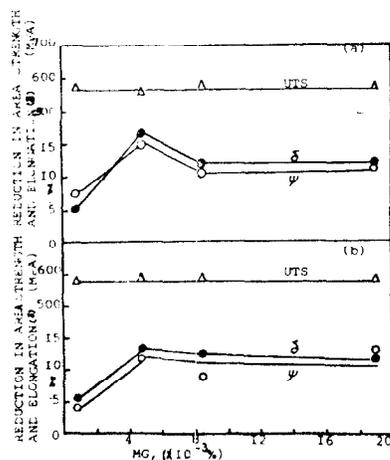


Fig.1 Effect of Mg on 950°C tensile properties of GH220 alloys before(a) and after(b) 1200hrs exposure at 850°C.

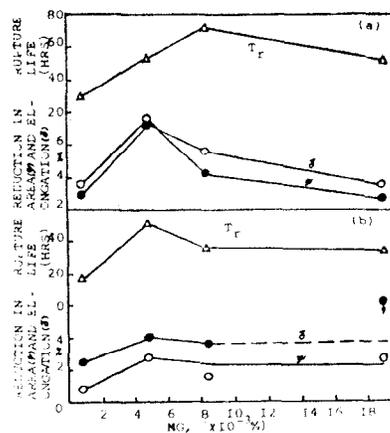


Fig.2 Effect of Mg on 940°C/216 MPa stress rupture properties of GH220 alloys before(a) and after(b) 1200hrs exposure at 850°C.

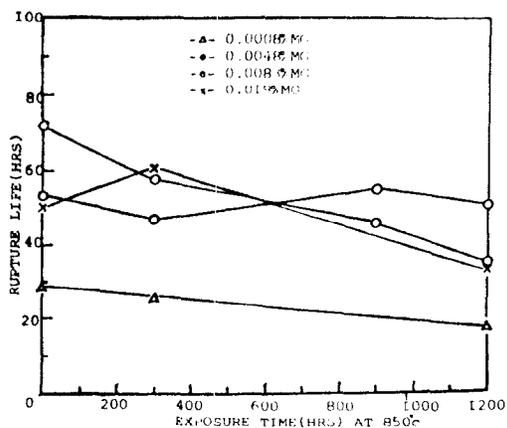


Fig.3 Effect of long time exposures at 850°C on stress rupture lives at 940°C/216MPa in GH220 with various contents of Mg.

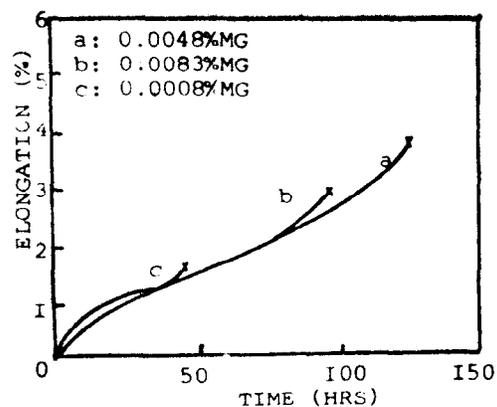


Fig.4 Effect of Mg on the 850°C/343 MPa creep behaviour of GH220 alloys after 1200hrs exposure at 850°C.

secondary stage creep, develop tertiary stage creep. The total elongation of secondary stage creep and creep fracture time are both increased. This tendency is still kept in function after 1200hrs exposure at 850°C. Creep test results also indicate that over addition of Mg in GH220 will decrease creep properties.

The influence of Mg on mechanical properties of GH169

It is shown in Fig.5, Mg-contained alloy GH169 possesses higher yield and ultimate strengths at ambient temperature, but this beneficial effect has been quickly vanished by long time exposure at 650°C. The Mg effect on stress rupture properties at 650°C is shown in Fig.6. Magnesium addition in GH169 can prolong stress rupture life and increase stress rupture ductility. The alloy with 0.0094% Mg is gradually softened during long time exposure at 650°C, therefore the stress rupture life is decreased and the ductility is increased mildly. However the stress rupture life and ductility of this alloy are still better than those of alloy with 0.0001%Mg.

Magnesium addition also has significant influence on creep properties. Typical creep curves are shown in Fig.7. The influence of Mg on steady-state creep rate is not significant, but Mg addition can substantially prolong secondary stage creep and pronouncely develop tertiary stage creep. The stress exponentials n in Bailey-Norton creep equation at 650°C are 18 and 27 for alloys with 0.0094% Mg and 0.0001% Mg respectively. Magnesium addition does not affect the creep activation energies of two alloys mentioned above which are 137.5 and 133.5 kcal/mol respectively.

The influence of Mg on microstructure of alloys

Microstructure of GH220 under normal heat treated condition contains 40-45wt% γ' phase, grain boundary carbide M_6C , boride M_3B_2 particles and random distributed primary block inclusions $Ti(CN)$. Complex phase analysis results on morphology, distribution, amount and composition of different phases show that the main effect of Mg on microstructure in GH220 is the change of grain boundary phase (mainly M_6C) morphology. Grain boundary M_6C particles of alloy with 0.0001% Mg are coarser and those of alloy with 0.0094% Mg characterize as finer globules (see Fig.8). This kind of structure difference is still kept up to 1200hrs exposure at 850°C. Magnesium addition almost has no influence on crystallographic characters of M_6C carbide and γ' phase. For alloys with and without Mg the crystallographic parameters of M_6C are 11.0778Å and 11.0772Å respectively and the average edges of cubic γ' are about 2500-3000Å.

The influence of Mg on microstructure in GH169 is similar to GH220 and structure change is also concentrated at grain boundary areas. There are a lot of $\delta-Ni_3Nb$ cellular precipitates at grain boundaries of alloy without Mg (see Fig.9), but only a small amount of block phases at grain boundaries of Mg-contained alloy and a number of $\delta-Ni_3Nb$ phases have been transferred to precipitates in the grains (also see Fig.9). Magnesium does not significantly affect γ'' size in these two alloys, the average diameters of γ'' discs are about 360Å under normal heat treated condition and about 1000Å after 5000hrs exposure at 650°C.

The segregation of Mg at grain boundaries

The distribution of Mg at grain boundary surfaces was determined by AES. There is significant segregation of Mg at grain boundary surfaces

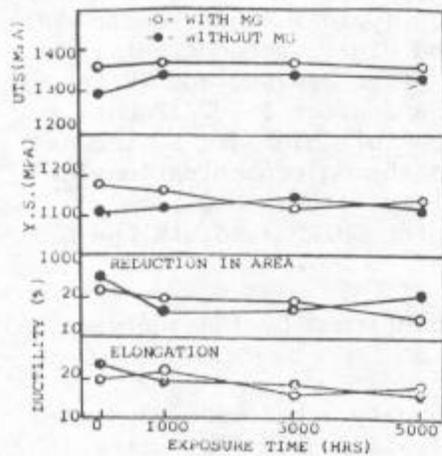


Fig.5 Effect of long time exposures at 650°C on ambient temperature tensile properties of GH169 alloys with and without Mg.

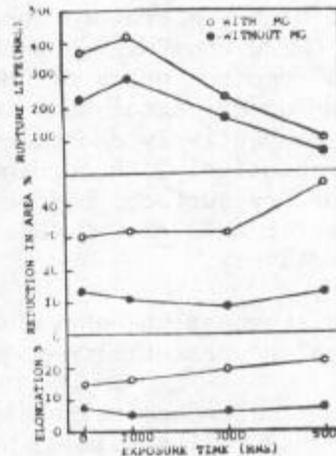


Fig.6 Effect of long time exposures at 650°C on 650°C/686.5MPa stress rupture properties of GH169 alloys with and without Mg.

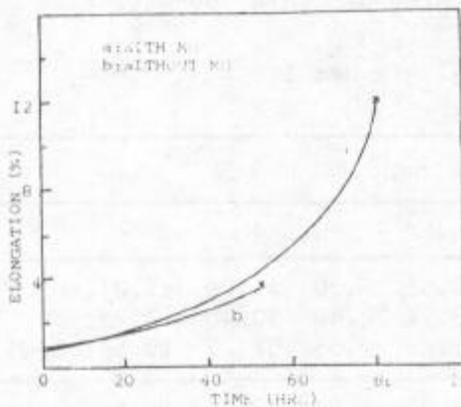


Fig.7 Effect of Mg on 650°C/735.5MPa creep behaviour of GH169 alloys after 5000hrs exposure at 650°C.

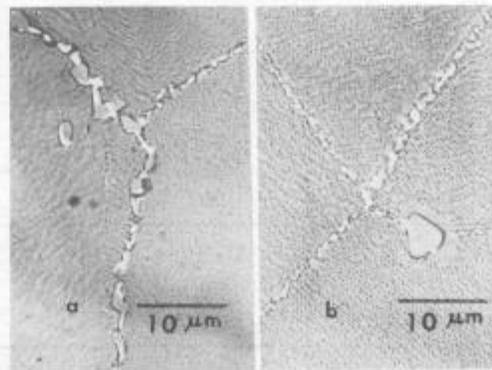


Fig.8 The influence of Mg on morphology of grain boundary carbides in GH220 without Mg (a) and with 0.0048% Mg (b).

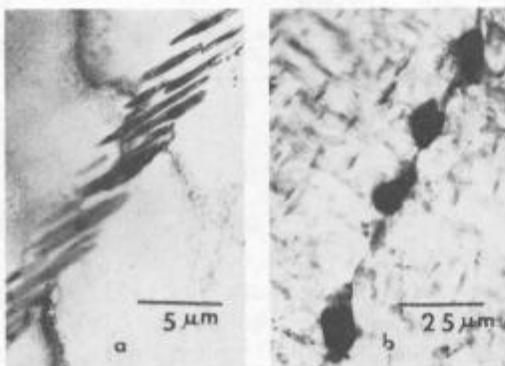


Fig.9 The influence of Mg on grain boundary δ -Ni₃Cb precipitation in GH169 without Mg (a) and with 0.0094% Mg (b).

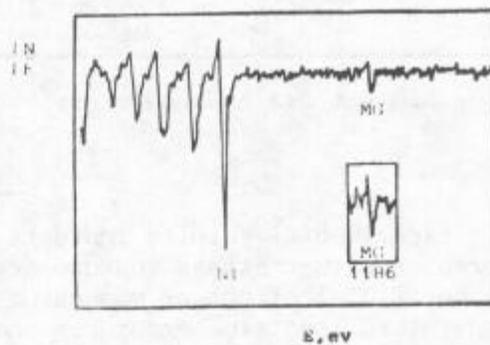


Fig.10 Typical Auger spectrum of intergranular fracture surface of GH220 with 0.019% Mg after 1200 hrs exposure at 850°C.

either in GH220 or in GH169 alloys both under normal heat treated condition and after high temperature long time exposures. Typical Auger spectra of modified GH220 and GH169 are shown in Fig.10 and Fig.11 respectively. Magnesium spectrum peaks of GH220 are vanished after 230 sec and 70 sec sputtering under normal heat treated condition and after 850°C/1200hrs exposure respectively and relevant magnesium peak of GH169 are 80 sec and 60 sec respectively. According to AES analyses the Mg concentrations at grain boundary surfaces before and after high temperature long time exposures for GH220 are 0.49 at% and 1.50 at%, for GH169 3.46 at% and 8.31 at% respectively.

This segregation behaviour of Mg is also confirmed by IMA analyses, its typical representative is shown in Fig.12.

Direct microchemical analyses at grain boundary areas were conducted on GH169 thin foil specimens by X-ray microanalysis in TEM for further confirmation and determination of Mg segregation behaviour. These data are shown on Table II. It can be seen in Table II that concentration of Mg at grain boundaries increases almost a factor of 10^2 in comparison with that in matrix. It seems to be considered that the Mg segregation is more serious at MC carbide/ γ matrix interfaces than at MC carbide free grain boundaries, but primary bulk Ti(CN) does not contain magnesium. It is valuable to indicate that Nb is also concentrated at grain boundaries.

Table II. Micro-chemical Analysis Results

Specimen Analysis		Chemical Composition wt%								
state	spot	Mg	Cr	Al	Ti	Mo	Nb	Ni	Fe	Si
Normal Heat-treated	G.B.+	0.31	20.95	0.20	1.07	2.61	4.90	51.06	19.01	0.25
	δ -Ni ₃ Nb		3.81	-	5.55	3.11	14.40	70.40	2.73	-
	G. ++		22.60	0.39	1.40	1.69	2.55	51.27	19.88	0.21
Normal Heat-treated +650°C/5000hrs/A.C.	G.B.	0.49	18.78	0.54	0.85	3.52	4.90	52.06	18.86	-
	G.		20.59	0.09	0.44	3.63	4.25	52.16	18.78	-
	G.B.with MC	0.80	20.83	0.68	4.46	7.47	30.25	24.80	9.66	1.06
	MC+G.B.	0.77	3.69	1.08	9.89	1.42	69.75	9.84	3.58	-
	MC in G.	1.38	14.38	1.47	3.84	2.76	27.35	33.70	13.88	1.21
	Primary MC	0.63	1.64	1.14	9.63	0.90	80.96	3.58	1.52	-
			1.84	1.23	10.11	2.07	78.54	4.37	1.83	-

+ G.B.-at grain boundaries; ++ G.-in grains

Discussion

Experimental results indicate that Mg addition in GH220 and GH169 increases either stress rupture and creep strengths or rupture ductility. The beneficial effect of magnesium is kept in function even after high temperature long time exposures and gradually weakened during exposure. The optimum amount of Mg addition for getting the highest strength and ductility improvement is moved to lower content of Mg after high temperature long time exposure. The mechanical properties of alloys with and without magnesium are getting closer after long time exposures. Under or over-addition of Mg in both alloys will intensively decrease stress rupture life after long

time exposures. There existed an optimum addition of Mg for keeping its beneficial effect. Therefore it is not reasonable to determine optimum Mg addition for long time service superalloy just from the view point of stress rupture and creep property improvement under normal heat treated condition. The long time exposure effect must be undertaken in consideration.

The main beneficial effect of Mg addition in both alloys is that Mg can obviously prolong secondary stage creep and highly develop tertiary stage creep. It can either prolong tertiary stage creep or increase ductility at fracture, but has no essential effect on steady-state creep rate and activation energy of creep. Substitution of small amount of Mg for Co can compensate stress rupture life and improve ductility but can not balance creep strength (steady-state creep rate). Therefore, the replacement of cobalt should not only rely on the magnesium addition which improves stress rupture life and ductility, but also the supplementary addition of other elements which improves creep strength, i.e. decreases steady-state creep rate. The role of cobalt in superalloys is to decrease steady-state creep rate and simultaneously prolong life to fracture (1-5). The Mg effect can retard creep crack initiation, decrease creep crack propagation then prolong the total creep life to fracture. As shown on SEM fractographs (see Fig.13) there are many fine dimples on the intergranular fracture surfaces of creep specimens with magnesium. Experimental results have confirmed that the substantial effects of magnesium on creep in GH169 and GH220 are same and there is a similar strength and ductility improvement mechanism, though they are two different kind superalloys.

Structural analysis results indicate that the influence of Mg addition in both alloys is the concentration of Mg at grain boundary areas, thus results in structure change at grain boundaries. Magnesium addition in GH169 can depress δ -Ni₃Nb cellular precipitation at grain boundaries and in GH220 can refine grain boundary globular MgC carbides. In this investigation Mg-rich phase has not been detected yet. In the range of sulfur content (0.005-0.007%) in this investigation Mg addition in both alloys can not affect the sulfur Auger spectrum peak significantly. Except these, magnesium addition also has no significant influence on main strengthening phases γ' and γ'' . It can be considered, main reasons of stress rupture life and ductility increments are the segregation of Mg itself at grain boundary areas and the improvement of grain boundary phase morphology and its distribution. This characteristic structure character resulting from Mg addition in both alloys is still remained after long time exposures. Magnesium addition in both alloys has no significant influence on the coagulation rate of γ' and γ'' during long time exposures.

AES analysis results show that the concentration of Mg at grain boundaries characterizes as equilibrium segregation. It can be seen from Fig.14 that magnesium has been further concentrated at grain boundaries during long time exposure, i.e. Mg content at grain boundaries increases after long time exposures. For instance, Mg contents at grain boundaries for GH220 before and after 850°C/1200hrs exposure are 0.49 at% and 1.50 at% respectively and for GH169 before and after 650°C/5000hrs exposure are 3.46 at% and 8.31 at% respectively. Simultaneously, the Mg segregation layer has been gradually thinned during long time exposures. Furthermore, in comparison of Mg concentration at grain boundaries of two kind superalloys, segregated content of Mg at 650°C in GH169 (8.31 at%) is much higher than that at 850°C in GH220 (1.50 at%). It is in agreement with equilibrium segregation theory. According to Mclean's theory (15), the equilibrium segregation equation is given by

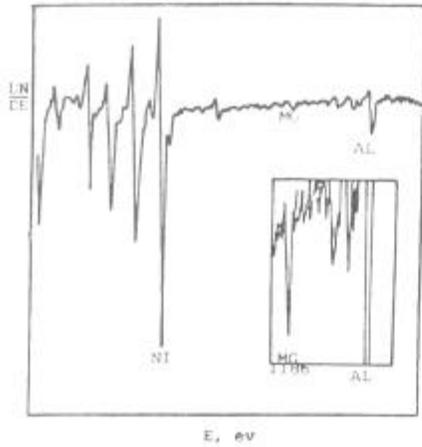


Fig.11 Typical Auger spectrum of intergranular fracture surface of GH169 with 0.0094% Mg after 5000hrs exposure at 650°C.

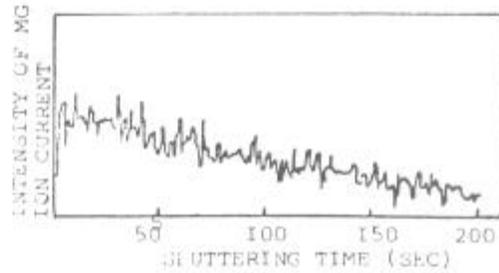


Fig.12 The change of Mg content with depth under the fracture surface obtained by IMA.



Fig.13 The influence of Mg on fracture mode of GH220 and GH169 alloys
 (a) GH220 without Mg, (b) GH220 with 0.0048% Mg,
 (c) GH169 without Mg, (d) GH169 with 0.0094% Mg.

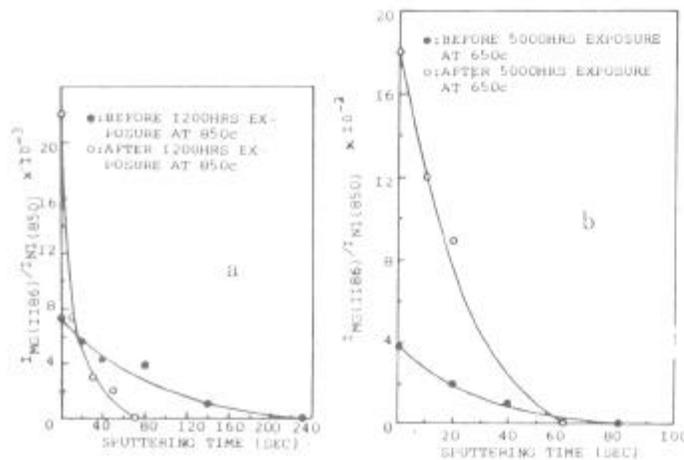


Fig.14 Depth-Mg relative content profiles of GH220 with 0.019% Mg (a) and GH169 with 0.0094% Mg (b) before and after long time exposure.

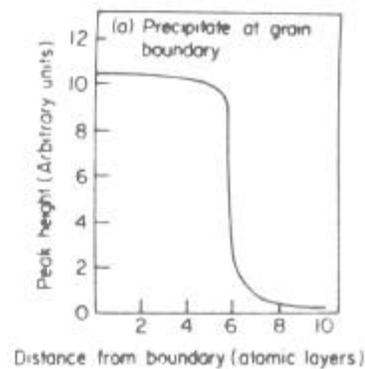


Fig.15 Typical AES sputtering profile of fracture surface covered by precipitates.

$$\frac{C_b}{C_{b0}-C_b} = \frac{C}{1-C} \exp\left(\frac{\Delta G}{RT}\right) \quad (1)$$

where C_b and C are magnesium content at grain boundaries and in the grains respectively, C_{b0} saturated concentration of Mg at grain boundaries for single atom layers, ΔG activation energy of segregation, T absolute temperature k and R gas constant. Segregation activation energies can be estimated (when $C_{b0}=0.33$) from equation (1) 51KJ/mol and 62KJ/mol for GH220 and GH169 respectively. However, these calculated data are not precise enough, but give us a clarified feature that magnesium is susceptible to segregate at grain boundaries. The activation energy of Mg segregation in superalloys is higher than that in plain steels and is equivalent to that of P segregation in highly alloyed steels (16). In comparison of Mg concentration at grain boundaries before and after long time exposure, it is shown that the segregation rate of Mg at grain boundaries is quite slow. The equilibrium will not be obtained even for several thousand hours exposure at 650-850°C. According to Mclean's kinetic theory of equilibrium segregation (15,16), the segregation kinetic equation can be simplified as:

$$Y(t) \approx 2(C/d) (Drt/\pi)^{\frac{1}{2}} \quad (2)$$

$$\text{and } Y(t) = X_b(t) - X_b(0) / X_{b0} - X_b(0) \quad (3)$$

where $X_b(0)$, $X_b(t)$, X_{b0} are grain boundary concentrations of Mg at the beginning, time t and time for saturation respectively, C concentration of Mg in grains, d the thickness of segregation layer in the grain boundary areas and D bulk diffusion coefficient. From equation(2) it can be suggested that the main reason of very slow segregation rate of magnesium is the very low content of magnesium. Thus, an important viewpoint can be derived that the segregation rates of all minor elements are very slow because of their small amounts. If the content of segregated elements increases, the time reaching equilibrium segregation will be decreased by a factor of square power. It can be deduced that if the minor element characterizes as an equilibrium segregation element, its effect will be kept in function during high temperature long time exposure. The segregation degree and its effect on relevant properties will decrease with the temperature increment.

It is clear from Fig.14 that the concentration of Mg decreases gradiently far from grain boundary. The gradual change of Mg content shows that Mg does not exist in grain boundary phases. Otherwise, it should be sharply changed as schematically shown in Fig.19(19). Ultrafine beam microanalyses direct on thin foil specimen in TEM confirm no existence of Mg in bulk Ti(CN). It is suggested that solution of Mg with larger atomic radius in the grain boundary areas will decrease vacancy density and simultaneously the diffusion coefficient of vacancies. The initiation and propagation rate of creep voids are proportional with grain boundary diffusion coefficient (17,18), therefore the segregation of Mg at grain boundaries should retard the initiation and propagation of creep voids. In the result of Mg effect on decreasing surface energy, magnesium characterizes as equilibrium segregation at grain boundaries. Because of surface energy change by Mg addition, the morphology and distribution of grain boundary phases can be changed. Thus, Mg addition in GH220 and GH169 can refine MgC carbides and depress δ -Ni₃Nb cellular precipitation respectively. These structural changes will decrease stress concentration at interfaces or grain boundaries during creep, therefore prolong secondary and tertiary stage creep and simultaneously increase the ductility at fracture.

Conclusions

1. Small amounts of Mg addition in GH169 and GH220 can improve stress rupture and creep properties not only under normal heat treated condition but also after 650°C/5000hrs and 850°C/1200hrs exposures respectively, but the optimum amounts of Mg addition in both alloys are moved to lower contents of Mg in comparison with normal heat treated alloys.

2. Magnesium effect on prolonging secondary stage creep and developing tertiary stage creep results in increment of stress rupture life and ductility by a factor of 1.5-2.5 and 2-3 respectively, it is illustrated by the retarding of creep void initiation and propagation.

3. The beneficial effect of Mg is segregation at grain boundaries and improvement of grain boundary phases, i.e. refinement of MgC carbide in GH220 and depression of δ -Ni₃Nb cellular precipitation at grain boundaries in GH169.

4. The concentration of Mg at grain boundaries characterizes as equilibrium segregation, the Mg equilibrium has not been reached after 850°C/1200 hrs exposure in GH220 and 650°C/5000hrs exposure in GH169. The reason of very slow segregation rate is that Mg contents in both alloys are very small.

5. Small amounts of Mg addition in superalloys can partly compensate the beneficial effect of Co on stress rupture improvement, but it is necessary to have a supplementary addition of other elements with Mg for decreasing steady-state creep rate.

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