DEVELOPMENT OF Co-FREE Ni-BASE SUPERALLOY FOR HTGR

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ABSTRACT

A study has been made of the development of a new solution strengthening type Co-free Ni-base superalloy which can be used for heat exchanger tube in high temperature helium gas cooled reactor.

The effects of Cr, W and Mo as solution strengthening elements for austenite matrix and of Y and Zr as grainboundary affecting elements on the creep rupture strength and on the microstructure of Ni-base superalloys have been investigated. As for the matrix composition, 18%Cr-15%W-0.5%Mo-Ni is found to be optimum. Creep rupture strength of this alloy is improved by the addition of proper amounts of Y and Zr. The maximum creep rupture strength is obtained when $S_Y(=([S]+2[O])/(0.5[Y]+0.1[Zr]))$ is nearly 1. The alloy composition is determined as follows ; 18%Cr-15%W-0.5%Mo-0.02%Y-0.02%Zr-0.05%Al-0.2%Ti-Ni. The creep rupture strength of this alloy in helium environment simulated in HTGR is comparable with that in air at 1000°C at 3.5 kg/mm².

Introduction

The utilization of nuclear heat from a high temperature helium gas cooled reactor (HTGR) is planned in order to develop the nuclear steelmaking which is now being investigated as a national project in Japan. To succeed in this project, a new structural heat resisting alloy having creep rupture strength more than 1 kg/mm^2 at 10^5 hours at 1000°C is required as a material of heat exchanger tube for HTGR.[1)]

This study is aimed to develop a new Ni-base superalloy used for the heat exchanger tube mentioned above. Generally, precipitation strengthening alloys are considered to be advantageous to obtain the required creep rupture properties.[2)] Those alloys, however, have many difficulties in the productivity of long size tube. Alloy design of new alloy is, therefore, based on the solution strengthening type because of good combination of properties of high strength at high temperature and significant formability, although some difficulties exist to achieve the required properties.

The alloy design is characterized by the good combination of matrix strengthening and grain boundary refining. Chromium(Cr), molybdenum(Mo) and tungsten(W) have been selected as the matrix strengthening elements. These alloying elements are expected to improve the high temperature creep rupture strength because of their low self-diffusion coefficient, high Young's modulus and large atomic size. In addition, yttrium(Y) and zirconium(Zr) have also been selected as the grain-boundary affecting elements, because of their strong affinity with sulfur (S) and oxygen(O). Cobalt(Co) is beneficial element in improving the creep rupture strength, but it is avoided because of its inductive radio activity.

Effect of these elements on, especially, creep rupture properties has been investigated.

Experimental Procedure

Since the creep rupture strength depends on the structural stability and it increases with decreasing the electron vacancy number Nv[3)], the range of alloy composition was selected so that Nv value was lower than 2.2. Nv value was calculated by Sim's method.[4)]

As the first step experiment, the materials for determination of optimum alloy composition of matrix were prepared by 500 g induction melting furnace in argon atmosphere. The nominal compositions of materials tested are shown in Table 1. These small ingots were hot-rolled and solution-treated at 1200°C for 60 min

The optimum alloy composition was determined by the creep rupture test at 1000°C at 3.5 kg/mm^2. The creep rupture properties of the optimum composition alloy was confirmed by

Table 1

Nominal chemical composition and calaculated Nv of tested alloy (0.07C-Ni balanced)

	Cr	Mo	W	Nv
1	18	0.5	9	1.59
2	18	0.5	12	1.69
3	18	0.5	15	1.74
4	18	3.0	6	1.66
5	18	3.0	9	1.71
6	18	6.0	6	1.74
7	18	6.0	9	1.78
8	18	9.0	6	1.81
9	22	0.5	9	1.78
10	22	0.5	12	1.87
11	22	0.5	15	1.92
12	22	3.0	9	1.87
13	22	3.0	12	1.94
14	22	3.0	15	1.98
15	22	9.0	3	1.95
16	22	9.0	6	2.00
17	22	9.0	9	2.05
18	22	12.0	3	2.02
19	22	12.0	6	2.08
20	22	15.0	3	2.12
21	22	15.0	6	2.16

Table 2

Chemical Compositions of tested alloy and calculated ΔS_Y.

	C	P	S	Cr	Mo	W	B	Zr	Y	O	ΔS_Y*
1	0.08	0.001	0.003	17.9	0.5	15.2	0.005	0.15	0.037	0.0006	0.13
2	0.05	0.001	0.004	18.2	0.5	13.7	0.005	-	0.064	0.0010	0.19
3	0.05	0.001	0.003	18.2	0.5	14.6	0.005	0.076	0.028	0.0009	0.23
4	0.07	0.001	0.003	17.6	0.5	15.0	0.005	0.070	0.021	0.0009	0.27
5	0.05	0.001	0.004	18.3	0.5	13.7	0.005	0.072	0.008	0.0006	0.46
6	0.06	0.001	0.005	18.0	0.5	14.0	0.005	0.052	0.022	0.0020	0.56
7	0.05	0.002	0.002	17.8	0.5	14.6	0.005	-	0.016	0.0017	0.67
8	0.07	0.002	0.005	18.2	0.5	14.5	0.005	-	0.020	0.0009	0.68
9	0.06	0.001	0.004	18.0	0.5	12.1	0.005	-	0.011	0.0005	0.91
10	0.05	0.002	0.006	18.1	0.5	14.2	0.005	0.087	-	0.0015	1.03
11	0.07	0.001	0.005	18.0	0.5	14.8	0.005	0.068	0.005	0.0025	1.28
12	0.08	0.001	0.005	18.4	0.5	14.3	0.005	0.065	0.005	0.0019	1.17
13	0.05	0.003	0.003	18.1	0.5	14.8	0.005	-	0.007	0.0010	1.43
14	0.08	0.003	0.008	18.0	0.5	13.6	0.005	-	0.006	0.0015	3.67
15	0.05	0.003	0.005	17.8	0.5	14.2	0.005	-	0.007	0.0064	5.09
16	0.07	0.001	0.003	17.9	0.5	14.5	0.004	0.02	0.016	0.0025	0.80

* $\Delta S_Y = \{[S] + 2[O]\}/\{0.5[Y] + 0.1[Zr]\}$

the material prepared by 10 kg vacuum induction melting furnace.

As the second step experiment, the effect of Y and Zr on the creep rupture properties of the optimum composition alloy determined by the first step experiment is investigated. The materials were prepared by 10 kg vacuum induction melting furnace. The chemical compositions of the materials are listed in table 2. The ingots were hot-rolled to plate followed by solution-treatment at 1200°C for 60 min or 1250°C for 60 min.

Creep rupture tests were carried out at 900, 1000 and 1050°C. Ductility change during long period of aging was also evaluated by Charpy test of subsize specimen at room temperature.

Optical and transmission electron microscopic observation, electron probe micro analysis (EPMA) and electron diffraction analysis were made to identify the precipitates.

Results

Determination of alloy composition

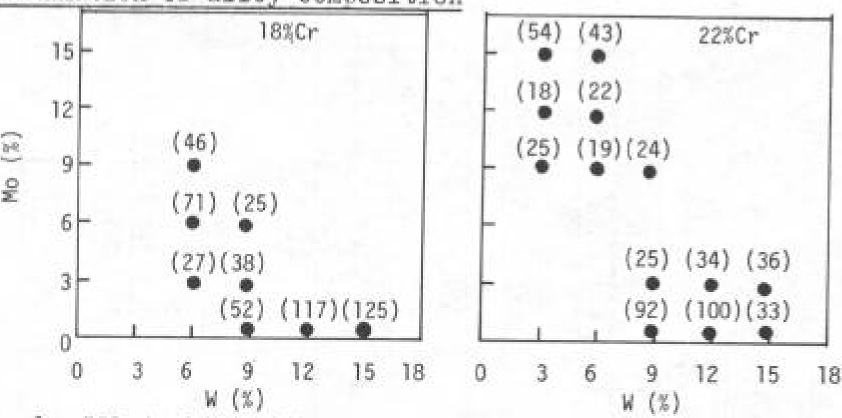

Fig. 1: Effect of Mo and W on creep rupture time at 3.5 kg/mm² at 1000°C in 18%Cr-Ni and 22%Cr-Ni alloys. Parenthesis number shows creep rupture time.

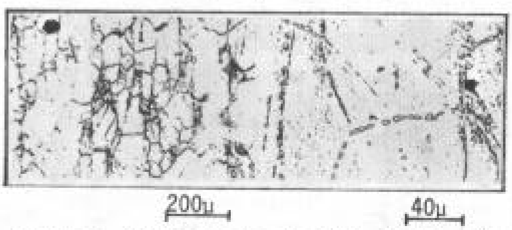

Photo 1: Micrographs of 18%Cr-15%W-.5%Mo Ni alloy heat treated at 1250°C for 60 min.

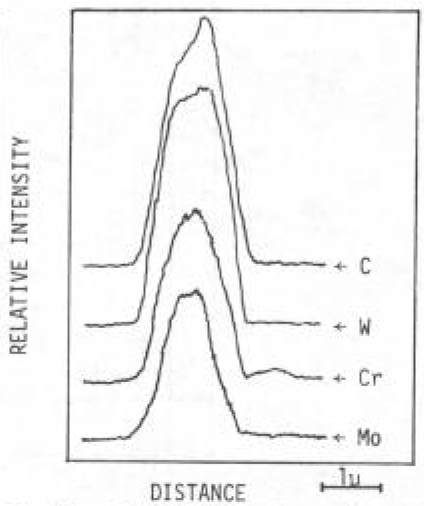

Fig. 2 : The relative intensity of Cr, Mo, W and C in the precipitates at grain-boundary in 18%Cr-15%W-0.5%Mo-Ni alloy.

The effect of Mo and W on the creep rupture time at 3.5 kg/mm² at 1000°C in 18%Cr-Ni and 22%Cr-Ni alloys are summarized in Fig. 1 It shows that 15%W with low level of Mo in the 18%Cr-Ni alloy has the longest creep rupture time. In case, the amount of Cr increased to 22%, the optimum amount of W moved to lower value, about 12% as shown in Fig. 1.

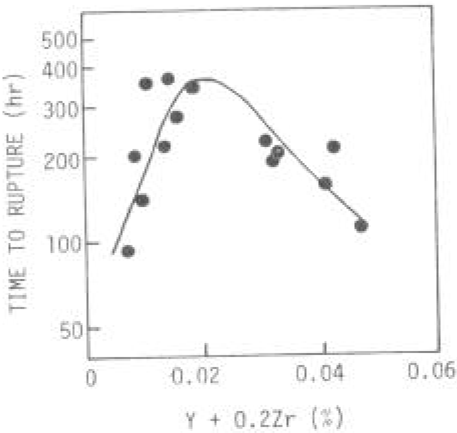

Fig. 3: Effect of Y and Zr on the creep rupture time at 4 kg/mm^2 at 1000°C.

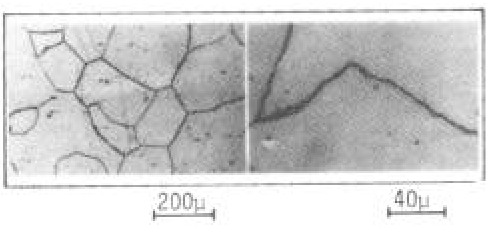

Photo 2: Micrographs of 18%Cr-15%W-0.5%Mo-0.02%Y-0.02%Zr-Ni alloy heat treated at 1250°C for 60 min.

Optical micrographs of 18%Cr-15%W-0.5%Mo-Ni alloy solution-treated at 1250°C for 60 min are shown in Photo. 1. The result of EPMA indicates that the grain-boundary precipitates are probably carbides which consist of Cr, W and Mo, as shown in Fig. 2.

The creep rupture strength of the 18%Cr-15%W-0.5%Mo-Ni alloy is improved by the addition of proper amounts of Y and Zr as shown in Fig. 3. It suggests that the best creep rupture strength is obtained when the value of Y + 0.2Zr (wt%) is about 0.02.

More precisely, this relation is rearranged by taking the S and O contents in the alloy into consideration, because both Y and Zr have strong affinity with S and O. Fig. 4 shows the relation between the creep rupture time at 4 kg/mm^2 at 1000°C and the atomic equivalent ratio of S and O to Y and Zr. It is found that the maximum creep rupture strength is obtained when

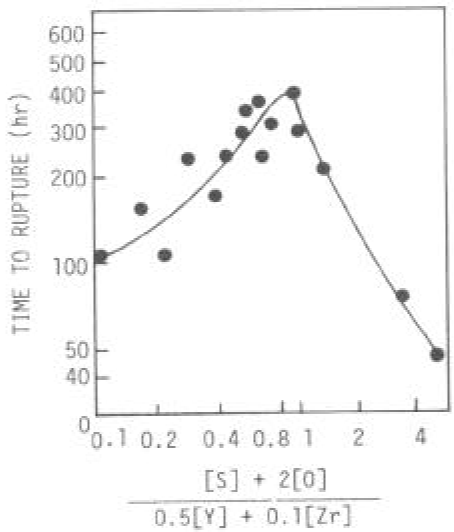

Fig. 4: Effect of Y, Zr, S and O on the creep rupture time at 4 kg/mm^2 at 1000°C

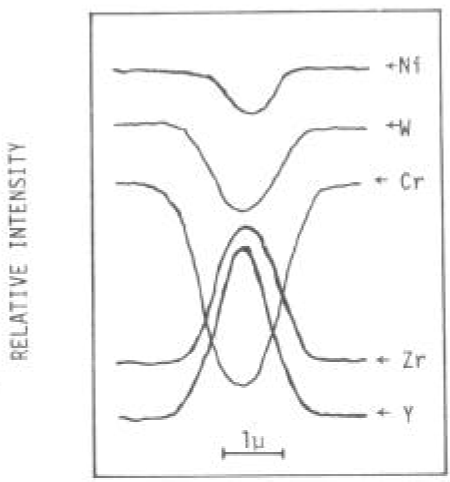

Fig. 5: The relative intensity of Ni, W, Cr, Zr and Y in the precipitates at grain-boundary in alloy 1 which contained the excess amounts of Y and Zr.

the following relation is satisfied,

$$\Delta S_Y = ([S] + 2[O]) / (0.5[Y] + 0.1[Zr]) \doteqdot 1$$

It implies that S and O are just fixed by Y and Zr as their sulfides and oxides in the matrix. When the excess amounts of Y and Zr are added, the formation of Ni-Y(Zr) intermetallic compound at grainboundary is observed as shown in Fig. 5 and the creep rupture time of the alloy is decreased.

Photo. 2 shows the typical optical micrograph of the alloy containing optimum amounts of Y and Zr against S and O contents (Sy=1). The size and morphology of the grainboundary precipitates are shown to be affected by the addition of Y and Zr as shown in the comparison between Photo 1 and 2. These precipitates are considered to be carbides containing W, Cr and Mo, and some of them are found to be surrounded by Y as shown in Fig. 6.

Generally, Al and Ti are beneficial elements to increase the creep rupture strength of Ni-base alloys. But in this study, the alloy is planned to be used in helium environment at high temperature. Under such circumstances, Al and Ti in the alloy are detrimental,because they increase the internal oxidation. Therefore their contents in the alloy were limited, and they only added to increase stabilize effect of Y and Zr on S and O.

Conclusively the alloy composition is determined as shown in table 3.

Table 3

Nominal chemical composition of selected alloy

C	Cr	Mo	W	B	Zr	Y	Al	Ti	Nv
0.07	18.0	0.5	15.0	0.005	0.02	0.02	0.02	0.2	1.75

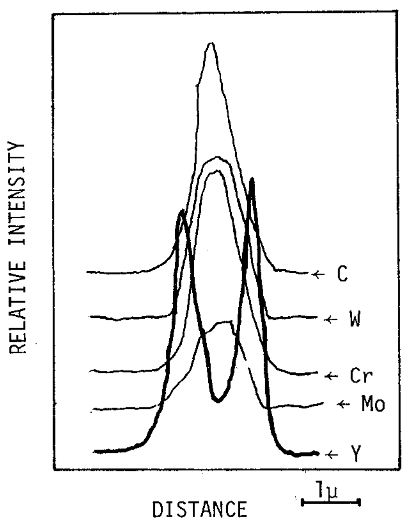

Fig. 6 : The relative intensity of Cr, Mo, W, C and Y in the precipitates at grainboundary in 18%Cr-15%W-0.5%Mo-0.02%Y-0.02%Zr-Ni alloy.

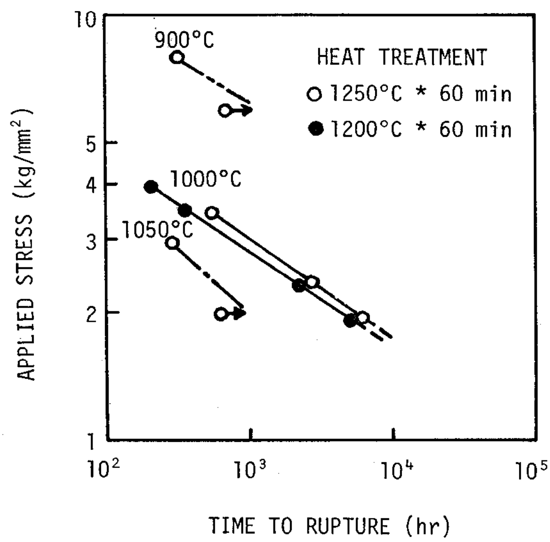

Fig. 7: Relation between applied stress and creep rupture time at 900, 1000 and 1050°C.

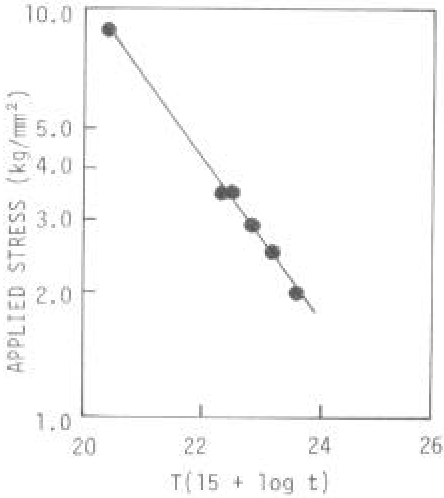

Fig. 8: Relation between Larson-Miller parameter and applied stress at 1000°C

Photo 3: Micrograph of creep ruptured specimen at 2.5 kg/mm^2 at 1000°C. Ruptured time is 2823 hours.

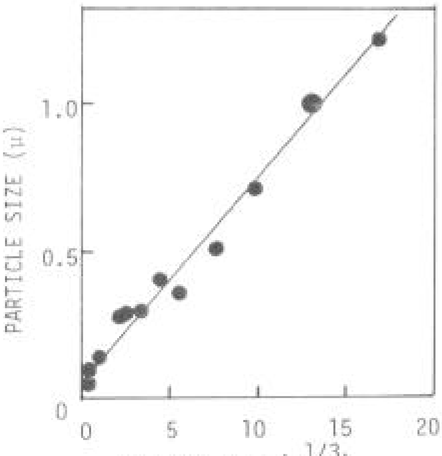

Fig. 9: Relation between the particle size of grainboundary carbide and heating time which is converted into 1000°C by Larson Miller parameter.

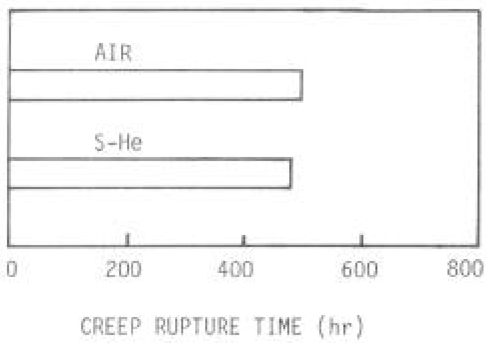

Fig. 10: Effect of helium atmosphere on the creep rupture time at 3.5 kg/mm^2 at 1000°C.

(S-He : 8 ppm H_2O-4 ppm Co_2-80 ppm CO-80 ppm H_2-8 ppm CH_4-8 ppm N_2-He)

Long period creep rupture property and aging behavior

The long period creep rupture test has been conducted for the alloy having the following composition as shown in table 4.

Table 4

Chemical composition of long period creep rupture test alloy

C	Cr	Mo	W	B	Zr	Y	Al	Ti	Nv
0.07	17.9	0.5	14.5	0.004	0.02	0.016	0.03	0.25	1.73

Fig. 7 shows the relation between applied stress and time to rupture at 900, 1000 and 1050°C in the alloy mentioned above. These results were rearranged by Larson-Miller parameter as shown in Fig. 8. The parameter constant of this alloy was 15 and the extrapolated creep rupture stress to 10^5 hrs at 1000°C was estimated to be approximately 1 kg/mm^2. The creep rupture occurred at grainboundaries, as shown in Photo 3. This photograph shows the optical micrograph of fracture region of the specimen which ruptured at 1000°C for about 2800 hrs. The specimen ruptured for a short time has a lameller type precipitates and one for a long time over 2000 hours has globular type coarsened precipitates only.

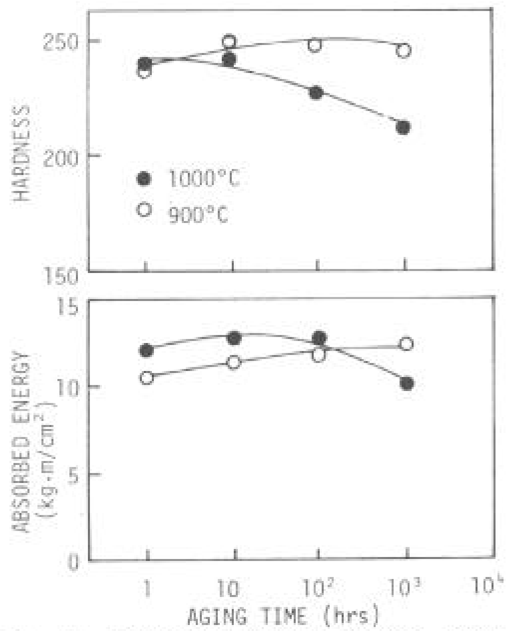

Fig. 11: Relation between hardness, absorbed energy and aging time at 900°C and 1000°C.

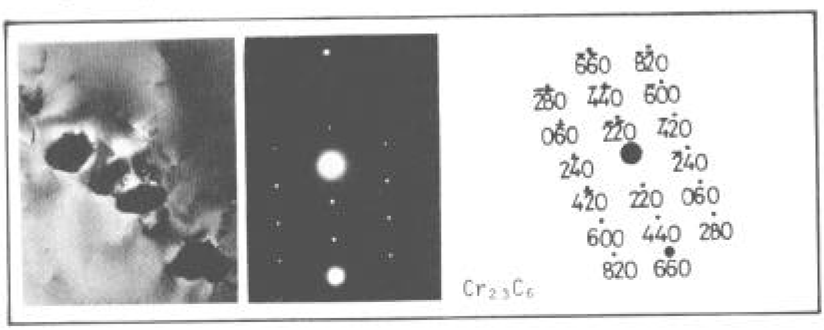

Photo 4: Electron diffraction pattern and the analysis of coarsened carbide at grain boundary.

Fig 9 shows the relation between the particle size of carbide at grainboundary and aging time ($t^{1/3}$). The aging time of specimens aged at various temperatures were converted to the aging time at 1000°C by Larson-Miller parameter. The growth rate of the carbide obeys the linear law of $t^{1/3}$ and the linear relation is held for long time such as 3×10^4 hrs.

The creep rupture property of the alloy in impure helium environment is illustrated in Fig. 10. The composition of impurity in helium was simulated with practical HTGR helium. It is obvious that the creep rupture time of the alloy in impure helium is about the same as that in air. It suggests that the creep rupture property of the alloy is not affected by this helium environment.

Fig. 11 shows the aging behavior of the alloy. It indicates that the change in room temperature hardness and absorbed energy with aging time at 900 and 1000°C. The change in hardness and ductility after aging at 900°C for 1000 hrs are very little. The aging at 1000°C for 1000 hrs results in slight decrease of the hardness and ductility. It can be noted that this alloy has good ductility after long period of aging at 900°C or 1000°C.

The slight decrease of hardness and ductility after aging at 1000°C for 1000 hrs is probably due to the growth of carbides at grainboundaries. The grainboundary carbide was analyzed by electron diffraction technique as shown in photo 4, and identified as $M_{23}C_6$.

It has been confirmed that this alloy can be hot-extruded and cold-drawn as a tube and also has significant weldability. The further study concerning the tube production will be presented in near future.

Discussion

A trial has been made on the development of solution strengthening type Ni-base superalloy (free from Co as alloying element) which is used for heat exchanger tube of HTGR. It is noted that the creep rupture strength of 1 kg/mm^2 at 10^5 hrs at 1000°C can be possibly obtained in a solution strengthening Ni-base alloy without containing Co.

This alloy is characterized by the addition of small amount of Y and Zr to improve the creep rupture strength. Generally Y is added to alloys in order to improve the oxidation resistance at high temperature. In this study, however, strong affinity of Y with S and O is utilized for the improvement of creep rupture strength. Namely, addition of Y is expected to catch S and O as its sulfide and oxide in the matrix and to prevent the grainboundary segregation of S and O which weakens the grainboundary strength during creep. Zr is also expected to have similar effect on S and O. As clearly shown in Fig. 4, addition of proper amounts of Y and Zr against S and O was confirmed to be very beneficial in improving the creep rupture strength of this type of Ni-base alloy. The maximum creep rupture time was obtained at the value of ΔSy was nearly 1. This fact suggests that the maximum creep rupture strength is obtained when S and O are just fixed by Y and Zr as their sulfides and oxides in the matrix and possibly grainboundary segregation of S and O is prevented. When the excess amounts of Y and Zr are added, the creep rupture time of the alloy is decreased. This result is probably related to the formation of Ni-Y(Zr) intermetallic compound at the grainboundary by the excess amounts of Y(Zr) as shown in Fig 5.

The alloy composition in this study is designed so that Nv value is smaller than 2.2 in order to maintain the stability of alloy structure at high temperature. The solution strengthening by alloying elements (Cr, W and Mo) was utilized to obtain good creep rupture strength of austenite matrix, and no precipitates except carbides were observed in the microstructure of the specimen ruptured at 1000°C at about 10^4 hrs.

The carbides in the matrix has the size of more than 1 μ in diameter in the solution treatment condition (before creep rupture test), and its growth was very small after the creep rupture test at 1000°C at about 10^4 hrs. The grainboundary carbides grow to about 1μ in diameter after the creep rupture test at 1000°C at about 10^4 hrs. Since the particle size affecting the creep rupture strength is considered to be smaller than 0.5μ[5], the strengthening effect by carbide precipitated either at matrix or grainboundary may be evaluated to be very slight in this alloy.

Conclusion

A new solution strengthening type Co-free Ni-base structural superalloy has been developed. The nominal composition of this alloy is 18%Cr-15%W-0.5%Mo-0.02%Y-0.02%Zr-0.05%Al-0.2%Ti-Ni.

The alloy is characterized by the addition of Y and Zr which are beneficial in preventing the segregation of S and O at grain boundary. The maximum creep rupture strength is obtained when ΔS_Y (=([S] + 2[O])/(0.5[Y] + 0.1[Zr])) is nearly 1.

The creep rupture strength of this alloy in helium environment simulated in HTGR is comparable with that in air at 1000°C at 3.5 kg/mm^2.

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