

# Development of the third generation single crystal superalloy for power generation gas turbines

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## ABSTRACT

For the purpose of developing the 3rd generation single crystal superalloy that can be applied to the power generation gas turbine, the single crystal superalloy that contains by about 5mass% Re was designed using the molecule orbit calculation of electronic structure that is based on the d-electrons concept.

As for designed single crystal superalloy, the influence of alloy element was examined on creep rupture strength and the oxidation resistance. Hot corrosion resistance and single crystal cast-ability were also studied in this work. Co, Cr, Ta and Re strongly influenced creep rupture properties and creep rupture strength improved when the Cr content decreased and Co, Ta and Re ones increased.

The other hand, Co, Re, Cr and Mo influenced an oxidation characteristic and it declined when the Cr content was little and Co, Re and Mo ones increased. Moreover, it was found that a little addition of Ce that is rare-earth element to improve oxidation resistance is very valid.

Designed single crystal superalloy has temperature capability\*<sup>1</sup> that is more than 20K higher than the 2nd generation single crystal superalloy. Also, it showed excellent hot corrosion resistance, and it was possible to cast single crystal bucket with 170mm in length. However, oxidation resistance of the designed superalloy was rather bad than the 2nd generation single crystal superalloy.

The development of the new 3rd generation single crystal superalloy has been carried, that is excellent oxidation resistance, based on this knowledge.

\*1: Temperature at 137MPa/100,000 hours creep rupture time

## 1. Introduction

To improve thermal efficiency of the gas turbine, it is the most effective to increase gas turbine inlet temperature. As for the latest gas turbine for the power generation, the gas turbine inlet temperature reaches 1800K. To increase gas firing temperature, single crystal buckets are used in the latest gas turbines. Single crystal superalloy was applied to commercial gas turbines in the second half of the 1970s and used as the vanes and blades of the jet engine for the aircraft because of its excellent heat resistance characteristics. Meanwhile, a lot of single crystal superalloys were developed.

Single crystal superalloy in the early stage of the practical use that is called the 1st generation single crystal superalloy doesn't include Re. After that, the alloy that is called the 2nd generation single crystal superalloys and contains 3mass% Re to improve the

creep strength was developed (Harris, et al., 1992). Moreover, recently, several kinds of the 3rd generation single crystal superalloys (contain 6mass% Re) and have more excellent creep strength, and hot corrosion resistance, than the 2nd generation single crystal superalloys are developed (Erickson, et al., 1996, Walston, et al., 1996 and Koizumi, et al., 1997), and they are used as the blade materials of the jet engine for the aircraft (Corman, 1995, Joyce, 1995 and Former, 1997).

However, all superalloys that are used for the power generation gas turbine are 2nd generation single crystal superalloys and any 3rd generation single crystal superalloys that are excellent creep strength and hot corrosion resistances are not commercially used.

Reasons why no 3rd generation single crystal superalloy is used for the bucket material are summarized as follows:

- 1) The material costs are high.
- 2) It is difficult to cast large size single crystal buckets.
- 3) At high temperature, the oxidation resistance is worse than the 2nd generation single crystal superalloys.

Therefore, it is necessary to solve these problems in order to apply the 3rd generation single crystal superalloys to buckets of the power generation gas turbine.

Therefore several kinds of superalloys which contain about 5mass% Re were designed for the purpose of developing the 3rd generation single crystal superalloy that can be applied to power generation gas turbines. Then, using those superalloys, the effects of alloy elements on creep rupture strength, and oxidation resistance were examined. And, hot corrosion resistance and single crystal castability were also evaluated.

## 2. Experimental procedure

Superior nickel based single crystal superalloys have been designed with the d-electrons concept. This concept has been devised on the basis of the molecular orbital calculation of electric structure (Yukawa, et al., 1988).

First, the ingot of the designed superalloy was created, and a single crystal specimen with the 15mm diameter length of 180mm was cast using mold with-drawal unidirectional solidification method. After casting, the single crystal specimen chemically polished and single crystal with no grain boundaries was confirmed by the watching inspection. Also, crystal orientation was measured by Back Laue method. Then, it used round bar of which deviation of the axis from <100> orientation was within 10°.

For each superalloy, the best solution heat treatment condition and aging heat treatment condition was choose based on the morphology of precipitated  $\gamma'$  phases after aging heat treatment. Then, all specimens were subjected to the solution heat treatment and aging heat treatment, and then creep rupture test, oxidation test and hot corrosion test were carried.

### 3. Alloy design

To apply the 3rd generation single crystal superalloy to the power generation gas turbine, it is necessary for the 3rd generation single crystal superalloy to have the same excellent properties as the 2nd generation single crystal superalloy or more. Therefore, following targets were set.

- 1) Have the temperature capability that is more than 20K higher than the 2nd generation single crystal superalloy.
- 2) Have the oxidation resistance that is similar to the 2nd generation single crystal superalloy.
- 3) Have the excellent castability to cast single crystal buckets.
- 4) Reduce Re content in the range where material cost can be decreased without harming high temperature properties.

Table 1 shows the composition of the single crystal superalloy that was designed by d-electron concept. As for deciding composition at candidate materials, the following criterion was set.

- 1) To maintain excellent hot corrosion resistance, it makes Ti more than 1.0mass% and it makes Cr more than 4.0mass%.
- 2) To facilitate solution heat treatment, it makes Al less than 5.6mass%.
- 3) Re content is reduced as low as possible to reduce the cost of the ingot without harming material properties. It makes the upper limit 5.5mass%.
- 4) To improve castability, it makes Ta content more than W content.
- 5) It makes the design parameter of Md and Bo the range of Md:0.98-0.99, Bo:0.655-0.665 respectively.

Table 1 Chemical composition of alloys studied(mass%)

alloy	chemical element(mass%)											Md	Bo
	Ti	Cr	Co	N	Mo	Hf	Ta	W	Re	Al	others		
A	1.8	6.0	1.0	Bal.	1.2	0.03	6.1	5.7	4.0	5.1	-	0.983	0.656
B	1.8	5.0	9.2	Bal.	1.2	0.03	6.1	5.7	4.0	5.1	-	0.983	0.663
C	1.0	4.2	2.2	Bal.	1.9	0.14	7.7	5.9	5.5	5.0	-	0.981	0.659
D	1.5	3.8	11.0	Bal.	1.4	0.14	6.7	5.3	5.4	5.1	-	0.983	0.664
E	1.3	4.2	4.7	Bal.	1.1	0.14	6.3	6.8	5.5	4.8	-	0.973	0.658
F	1.0	6.8	3.0	Bal.	1.6	0.12	6.5	6.4	3.8	5.4	-	0.989	0.669
G	1.4	5.0	11.0	Bal.	-	0.12	6.8	6.4	4.4	5.3	-	0.985	0.664
H	1.4	5.0	11.0	Bal.	0.5	0.12	6.5	5.6	4.4	5.3	-	0.982	0.662
I	1.0	3.8	11.5	Bal.	1.4	0.14	6.8	5.3	5.3	5.6	-	0.986	0.660
J	1.2	4.5	10.5	Bal.	1.0	0.12	6.8	6.0	4.4	5.5	-	0.987	0.662
K	1.2	4.0	11.0	Bal.	0.8	0.12	6.8	6.0	5.2	5.5	-	0.987	0.661
L	0.9	2.8	14.0	Bal.	1.4	0.12	7.0	5.5	5.5	5.6	-	0.984	0.659
M	1.5	4.0	11.2	Bal.	0.6	0.14	6.7	5.5	5.4	5.3	-	0.985	0.661
N*	-	3.0	12.0	Bal.	2.0	0.10	6.0	6.0	5.0	5.7	-	0.965	0.649
O*	1.0	6.5	9.0	Bal.	0.6	0.10	6.5	6.0	3.0	5.6	-	0.984	0.664
P*	0.7	6.6	9.2	Bal.	0.5	1.40	3.2	8.5	3.0	5.7	C:0.07 B:0.015	0.983	0.664

\*N~P:Reference alloy

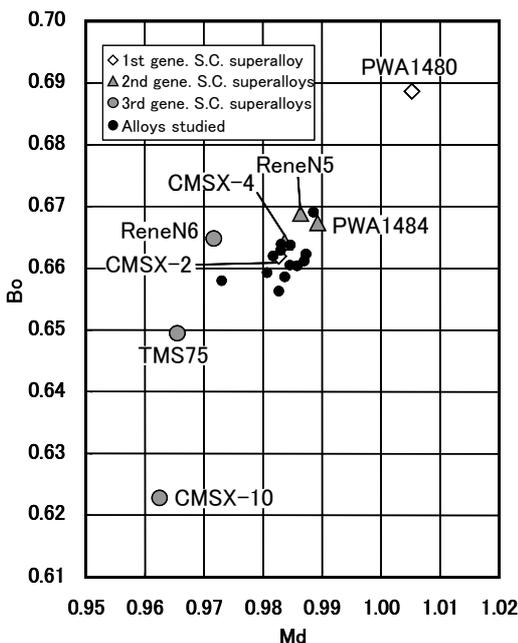


Fig.1 Bo-Md values of alloys studied.

In several kinds of superalloys, it didn't satisfy the design standard but it fixed composition by the whole balance.

It specified the range of Md that is a design parameter and Bo from the following reason. That is, in conventional casting superalloys, 0.2% yield strength and the creep rupture strength become maximum, when Md and Bo are about 0.98 and 0.67 respectively (Murata, et al., 1996.). Moreover, it is why the most the 1st and 2nd generation single crystal superalloy has 0.98-0.99 of Bo and 0.66-0.67 of Md (Matsugi, et al., 1992).

Fig.1 shows the Bo, Md value of designed alloys. The Md-Bo value of designed superalloys is nearly equal to that of CMSX-4. CMSX-4 is one of the most excellent materials of the 2nd generation single crystal superalloys. However, the Md-Bo value at the designed superalloy completely differs from that of the existing 3rd generation single crystal superalloy. It is one characteristic of the designed superalloy in this research.

### 4. Results and discussions

#### 4.1 Effect of Co on solution heat treatment

The 3rd generation single crystal superalloy includes a lot of alloy elements with lower diffusion speed and solute distribution coefficient of over 1.0, so that solution heat treatment takes a very long time. In the superalloy that is named CMSX-10, solution heat treatment time is 45 hours. On the other hand, in the superalloy that is named TMS-75, solution heat treatment time becomes very short and 6 hours. The biggest difference of the two alloys is Co content. Therefore, an influence of Co content on solution heat treatment was investigated by the superalloy A, B, C and D.

Fig. 2 shows the volume fraction of eutectic  $\gamma'$  phase as a function of solution heat treatment temperature in superalloy A, B, C and D. Alloy elements are same in superalloy A and B except Co content. Superalloy C and D have higher Re content than superalloy A and B, and superalloy C and D also have same amount of alloy elements except Co content. Comparing superalloy A with superalloy B, in superalloy A the temperature where the volume fraction of eutectic  $\gamma'$  phases begins to decrease and also the temperature of the incipient re-melting are about 20K higher than alloy B. Also, when comparing superalloys C, D and superalloys A, B, the tendency that the rate of eutectic  $\gamma'$  phase becomes small and the temperature of the incipient re-melting are the same as superalloys A and B approximately. It is impossible to solve eutectic  $\gamma'$  phase perfectly for 4 hours solution heat treatment in the four superalloys.

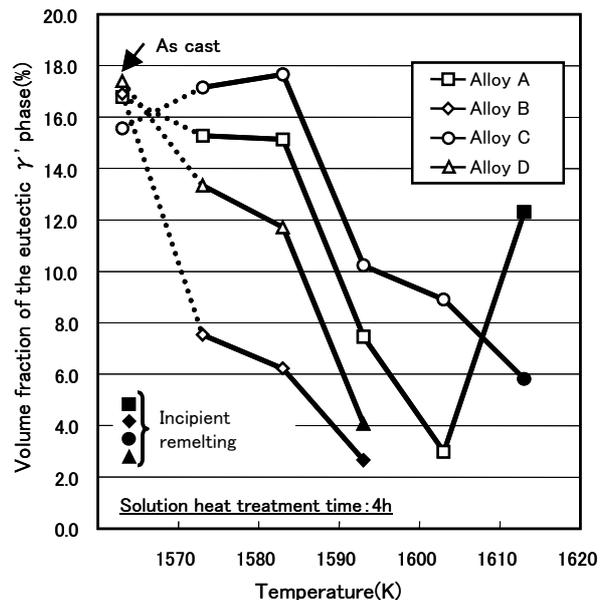


Fig.2 Effect of solution heat treatment on volume fraction of the eutectic  $\gamma'$  phase.

**Table2** Effect of heat treatment conditions on the solution of  $\gamma'$  phase.

alloy	solution heat treatment			
	SHT(1)	SHT(2)	SHT(3)	SHT(4)
A	△	○	× ×	-
B	◎	◎	×	-
C	△	△	× ×	× ×
D	◎	◎	×	-

◎: 100% solution  
 ○: Slightly remaining eutectic  $\gamma'$  phase  
 △: Remaining eutectic  $\gamma'$  phase  
 ×: Slightly incipient remelting  
 × ×: Incipient remelting

SHT(1): 1573K/12h+1583K/12h+1593K/24h  
 SHT(2): 1583K/8h+1593K/8h+1603K/8h  
 SHT(3): 1593K/8h+1603K/8h+1613K/8h  
 SHT(4): 1583K/12h+1593K/12h+1603K/12h+1613K/24h

The step solution heat treatment was conducted in superalloy A, B, C and D, where heat treatment temperature was increased from 1573K to 1613K by every 10K. Table 2 shows eutectic  $\gamma'$  solution behavior after the step solution heat treatment. It was found that the step solution heat treatment could not solve all eutectic  $\gamma'$  phase in superalloy A and C.

On the other hand, it could solve eutectic  $\gamma'$  phase completely in superalloy B and D. Superalloy B and D contain higher Co content than superalloy A and D, and it suggests that Co addition could accelerate eutectic  $\gamma'$  solution in the 3rd generation single crystal superalloy. Therefore, it is thought that the addition of Co is requested to facilitate eutectic  $\gamma'$  solution in the 3rd generation single crystal superalloy with Re high quantity. Eutectic  $\gamma'$  could be solved perfectly in superalloy E to M by the step solution heat treatment, because they might have higher Co content.

#### 4.2 Creep rupture strength

Creep rupture tests of designed superalloys were carried in the stress condition of 137MPa at 1313K, 206MPa at 1193K, 441MPa at 1123K respectively.

Fig.3 shows relationship between creep rupture lives of designed superalloy and Md, Bo. An effect of Md on creep rupture life is small in designed alloy except superalloy E of which Md value is low and superalloy A where eutectic  $\gamma'$  could not perfectly solved. On the other hand, creep rupture life becomes the longest at about 0.66 of Bo value. This Bo value is little smaller than value of conventional casting superalloys.

In the d-electrons concept Md and Bo Values depend on amount of each alloy element, however, even if it uses a parameter with the same value in the alloy design that is based on the d-electrons concept, it is possible to choose the quantity of each alloy element freely. Therefore, effects of alloy element on creep rupture strength were studied.

Fig.4 shows effect of alloy element on creep rupture lives. Creep rupture strength increases with increasing Co, Ta and Re. Addition of Co, Ta and Re tends to improve creep rupture strength effectively in 1123K and 1193K, however the effect of Co, Ta and Re on creep rupture strength cannot be observed clearly at 1313K of creep temperature. It was also found that creep rupture strength increases with decreasing Cr content in designed superalloy.

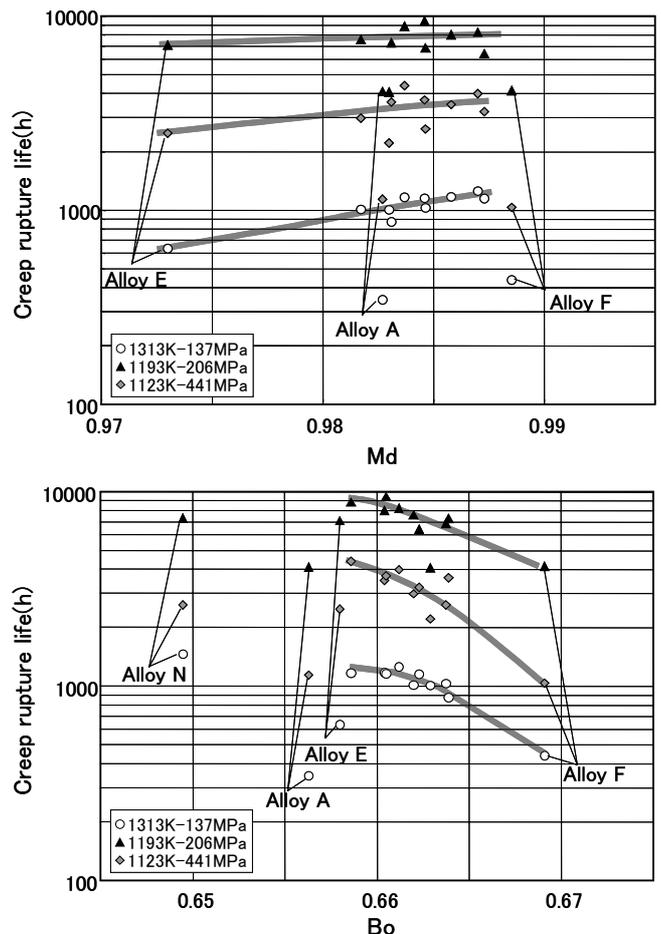
For the purpose of improving creep rupture strength, it is very important to add the higher Co, Re and Ta contents and also the lower Cr one in the designed superalloy. However, as shown at section 4.3, except for Ta, addition of Co and Re are harmful to oxidation resistance.

Therefore it is requested to optimize Co and Re contents in order to improve creep rupture without a reduction of oxidation resistance. According to Fig.4, superalloys having Re levels as much as 4.4mass% do not show a remarkable reduction of creep rupture strength. Therefore, it is very beneficial for the 3rd generation single crystal superalloy to have about 4.4mass% Re and the higher Ta levels in order to improve creep rupture strength. The Re and Ta levels above-mentioned are also effective to make a material cost inexpensive and also improve single crystal castability.

From the result of this study, it is thought that as much as 11mass% Co additions is necessary to facilitate solution heat treatment and also to improve creep rupture strength.

In the superalloys that were evaluated in this research, effect of Mo, Ti, W, and Al on creep rupture strength could not be confirmed. One reason why effect of Mo, Ti, W and Al to creep rupture strength are not clear is the narrow composition range of evaluated superalloy.

Fig.5 shows typical creep rupture strength of superalloy G and K. The creep strength of superalloy G is rather lower than superalloy K at high stress levels because of lower Re content. However, the temperature capability of superalloy G, projected by 137MPa/10<sup>5</sup>h condition, is equivalent to the superalloy K. Then, the temperature capability of superalloy G and K are about 110K higher than IN738LC and also about 20K higher than superalloy O, which is classified as the typical 3rd generation single crystal superalloy.



**Fig.3** Effects of Md and Bo on the creep rupture life.

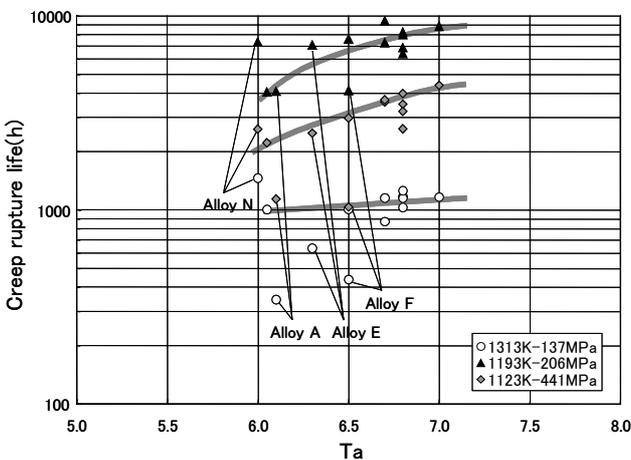
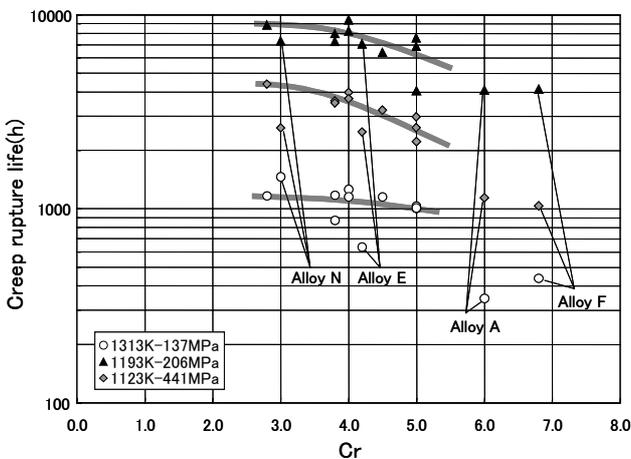
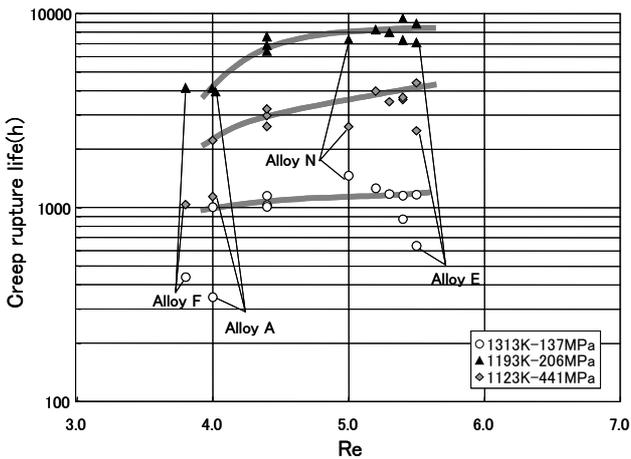
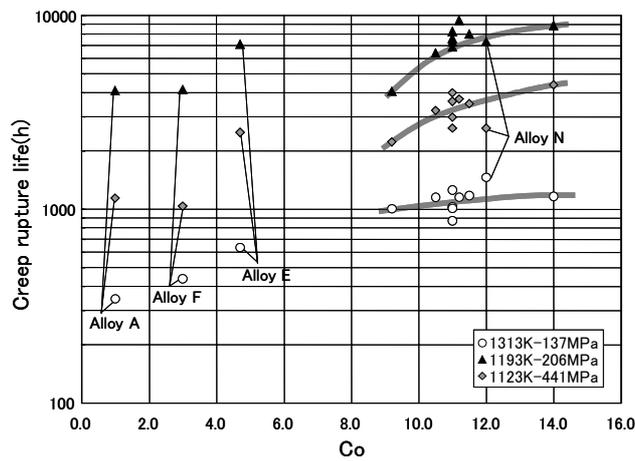


Fig.4 Effects of alloy elements on the creep rupture life.

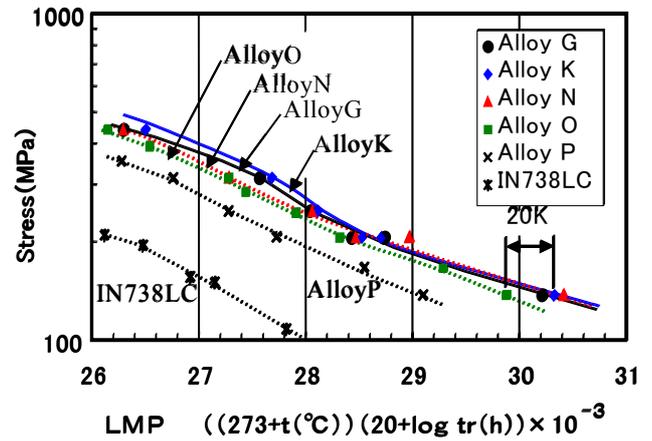


Fig.5 Creep rupture strength of alloy studied.

#### 4.3 Oxidation characteristic

To evaluate influences of alloy elements on the oxidation characteristic of the 3rd generation single crystal superalloy, the 3000h (5 times of 600h) oxidation tests was performed at 1313K using alloys shown in table 1 and weight changes were measured.

Fig. 6 shows influences of Co, Re, Cr and Mo on the oxidation. In designed superalloys except the superalloy E of with low Al levels and the superalloys G, H with low Re and low Mo levels, as the Co content increases, the oxidation becomes severe. From the result above, it found that the addition of Co accelerates the oxidation of the 3rd generation single crystal superalloy. Based on the result as shown in 4.1, the addition of Co is indispensable to facilitate solution heat treatment in the 3rd generation single crystal superalloy and also to improve creep rupture strength. It is very important to improve oxidation resistance in alloy with higher Co levels. Besides it was found that the oxidation resistance becomes bad rapidly when the Re content exceeds 3mass% in designed superalloys except alloys with low Co levels. Re is indispensable element to improve creep strength and hot corrosion resistance, and the high Re addition to single crystal superalloys is one characteristic of the 3rd generation single crystal superalloy.

Therefore, the improvement of the oxidation resistance must be attempted in alloy with high Re levels as well as Co. On the other hand, the oxidation resistance can be improved in the alloys with high Cr levels and low Mo ones. Specifically, the effect of Cr on the oxidation resistance is remarkable. Oxidation resistance is substantially improved in increasing Cr content to about 6 mass%. However, on increase in Cr content reduces creep rupture strength. It is necessary to optimize Co, Re, Cr and Mo contents not only for creep rupture strength but also for the oxidation resistance of the 3rd generation single crystal superalloy. It is not sure that other elements expect Co, Re, Cr and Mo evidently have some effect on the oxidation characteristic.

#### 4.4 Hot corrosion resistance

Fig.7 shows the hot corrosion test results of design superalloys. As for the comparative material, the commercial superalloys N to P were also tested. The test results showed that alloy L had the poorest corrosion resistance of the design superalloys. The Co content is higher than the other alloys in the alloy L, so that the oxidation resistance is bad in superalloy L. That might be why the hot corrosion resistance of superalloy L is much inferior to than the other alloys. The hot corrosion resistances at other design alloys are more excellent than superalloy N and P, and they have the hot corrosion resistance that is equivalent to superalloy O. These characterizations seem to be obtained by the high Re content. The test superalloys don't have Ce. Therefore, because a stable oxidation film is formed on the superalloy surface by the Ce addition as shown in section 4.5, it is expected that the hot corrosion resistance could be improved by adding Ce in design superalloys.

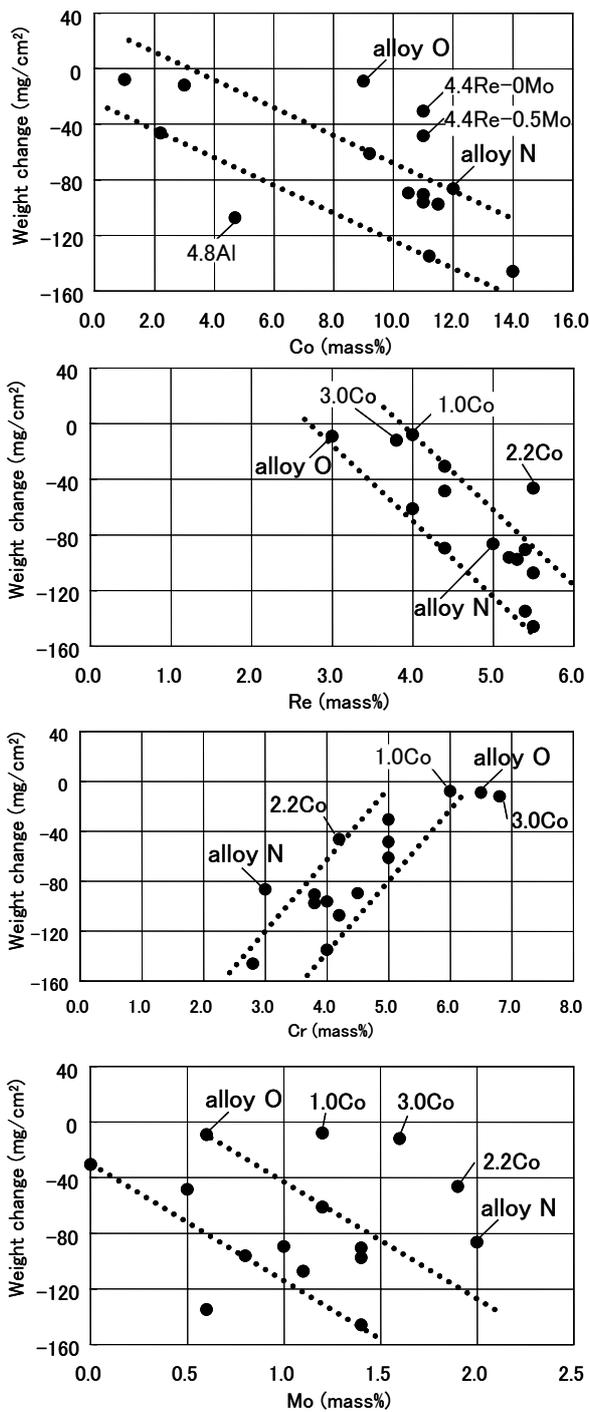


Fig.6 Effects of alloy elements on the weight change in oxidation tests.(1313K-3000h)

#### 4.5 Effect of rare-earth element

It is reported that adding rare-earth element can improve the oxidation resistance of the 2nd generation single crystal superalloy (Ford, et al., 1998). If addition of rare-earth elements improve the oxidation resistance of the 3rd generation single crystal superalloys with high Re levels independently, it is not necessary to take into account of other element addition to obtain excellent oxidation resistance. The effect makes it possible to choose adding elements and their adding levels widely in alloy design, and more superalloys having excellent high- temperature strength can be expected to develop based on the d-electrons concept.

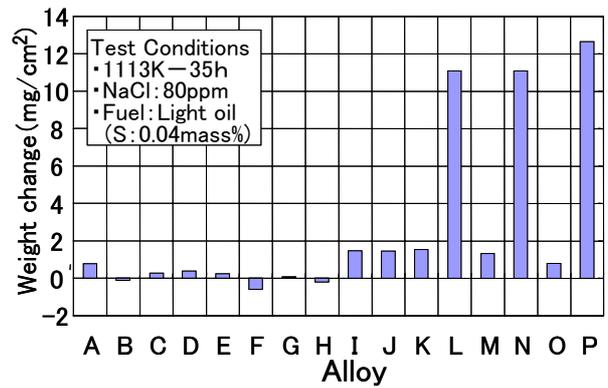


Fig.7 Overview of test specimens after burner rig tests and weight changes for the tests.

Fig. 8 shows the oxidation test results of the superalloy G that contained Ce by 30ppm and superalloy G without Ce. The tests were conducted for 240h (12 times of 20h) at 1373K and for 3600h (6 times of 600h) at 1313K respectively. In the superalloy without Ce, the weight of the specimens decreases with increasing exposure time. On the other hand, the weight increases of the specimens with 30ppm Ce are few and the weight changes are hardly observed. Then, the oxidation resistance of the superalloy at 1373K and 1313K is substantially improved by addition of Ce.

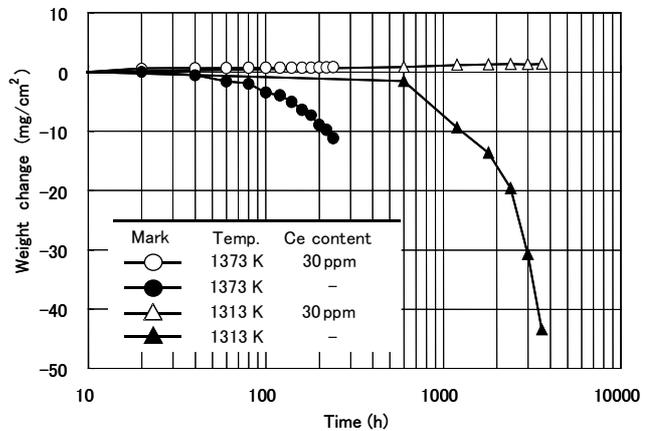


Fig.8 Result of oxidation test.

Fig. 9 shows a microstructure in the section of the oxidation specimen after tested for 240h at 1373K. The oxidation scale thickness of the specimen without Ce is about 50 $\mu$ m and has the 2-layer scale structure. On the other hand, the oxidation scale thickness of the specimen with 30ppm Ce is about 6 $\mu$ m, and moreover the number of layer in the scale structure is 4 layers.

Table 3 shows result of Semi-Quantitative EDX analyses in the oxidation scale that was formed on the superalloy surface. As for the scale of the specimen without Ce, the outer layer consists at the Ni-Co oxide, the inner is the Ni, Cr and the W+Ta oxide, and then stable oxide isn't formed on the surface of superalloy. On the other hand, as for the specimen with Ce, the oxide in the first outside layer is same as the specimen without Ce, and the oxide in the second and third layers structure has high Al content. Moreover, the content of the oxide in the forth layer is approximately 100 % of Al. It was found that high purity aluminum oxide was formed in the inner layers.

As for the improvement of the oxidation resistance by the Ce addition, the following reasons are expected from these results. In the superalloy without Ce, the stable and dense aluminum oxide isn't formed on the surface of superalloy. Therefore, the growth of the oxidation film and spall of the formed oxidation layer are repeated by thermal cycling and the oxidation progresses.

On the other hand, when adding Ce, the stable and dense aluminum is formed in the inner oxidation scale. Therefore, the penetration oxygen hardly occurs by the protective aluminum oxide scale and the oxidation doesn't progress. Also, because the oxidation scale is thin, the spalls of scale are prevented. Incidentally, the reason why a stable aluminum oxide film is formed in the Ce addition alloy isn't clear.

Figure 10 shows creep rupture strength of the specimen with Ce. In the specimen with Ce, on extreme decline of creep rupture strength isn't observed. It concludes that the Ce addition to the 3rd generation single crystal superalloy is valid to improve oxidation resistance without on extreme decline of creep rupture.

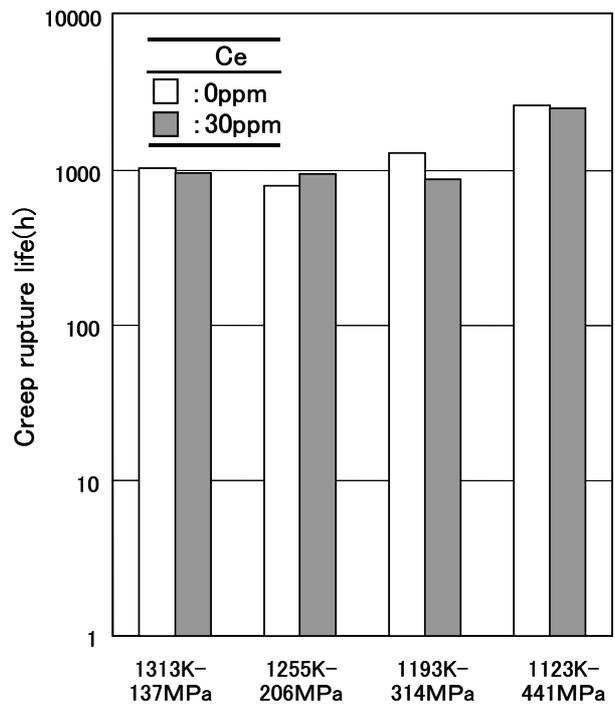


Fig.10 Creep rupture lives of the alloy G with Ce addition and Ce free alloy G.

As for the Ce addition, the stability of the Ce yield in the bucket is important. There are casting problem to solve in adding Ce, for example the securing of stable yield, the restraint of the reaction to the core material and so on. It is necessary in order to apply superalloys with Ce to the heavy-duty gas turbine bucket to develop various advanced technology.

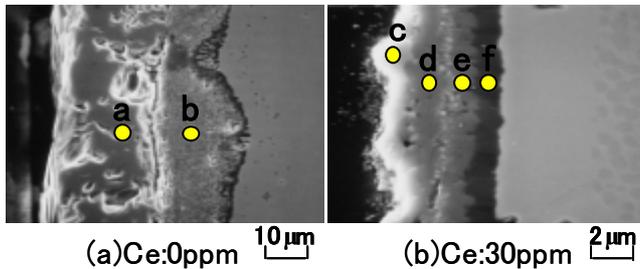


Fig.9 SEM micrographs of surface scale.

Table3 Semi-quantitative EDX analyses of surface scale after oxidation test.(mass%)

position	chemical element					
	Ni	Co	Cr	Al	Ti	W+Ta
a	79.1	20.9	-	-	-	-
b	26.5	8.1	16.6	8.6	2.4	37.8
c	92.0	6.0	2.0	-	-	-
d	36.7	9.6	13.2	37.1	3.4	-
e	33.7	8.5	7.8	47.5	-	2.5
f	-	-	-	100.0	-	-

#### 4.6 Single crystal casting in model bucket

The large-sized single crystal bucket casting is the most difficult problem to apply the 3rd generation single crystal superalloy to the power generation gas turbine. Generally, as Re and W of which the solute distribution coefficient is bigger than 1 increase, the single crystal casting becomes difficult. T. M. Pollock performed the casting test of the large-sized bucket by alloys with various Ta, W, and Re contents. Then, it showed that it was easy to single crystallize buckets when Ta was 9.0mass% (Pollock, et, 1992).

In this research, Ta/W ratio was made bigger than 1 to improve castability. For the purpose of assessing single crystal bucket cast ability, the casting test of the model bucket was carried out using superalloy K and then a cast bucket characteristics were evaluated.

The alloy composition, the bucket shape and the casting condition influence mainly on a single crystal bucket castability. As the standard single crystal castability evaluation method, the casting test of the single crystal bucket was conducted. As a result of the casting test, when the casting condition was improper, grain defects mainly occurred at the dubtail part. For example, freckle and an equiaxis grain flaw and so on could be observed at the area. The single crystal bucket could be cast successfully in making casting conditions appropriate and it was confirmed that the developed superalloy K could cast a single crystal bucket.

Fig.11 shows the single crystal model bucket trials cast. The model bucket has dimensions with 170 mm long and return-flow type cooling structure inside.

Next, the cast single crystal bucket was subjected to the solution heat treatment and aging heat treatment, and then a microstructure was observed.



Fig.11 Overview of trially casted model bucket.(length: 170mm)

Fig.12 shows microstructure in the three cut part of the single crystal bucket before and after solution heat treatment. Microstructure observations were conducted in three positions (A, B, C) of the bucket. Any microstructure variations are not observed in the three positions. Also, after solution heat treatment, the remainder of eutectic  $\gamma'$  phases and the incipient re-melting in casting are not observed and 100%  $\gamma'$  phase solution single crystal bucket can be obtained.

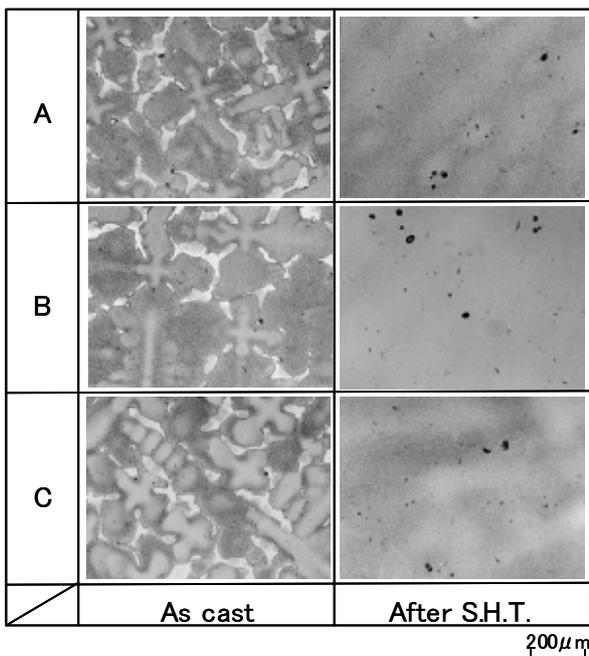
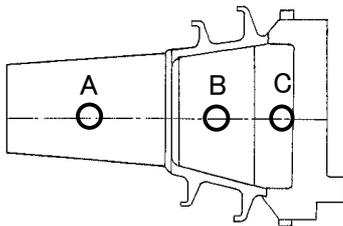
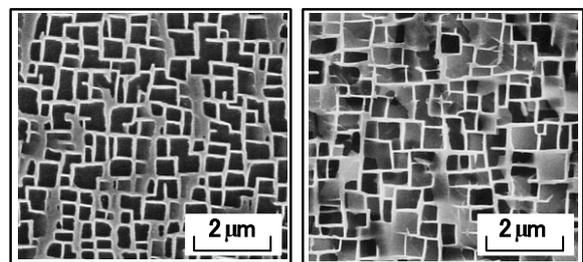


Fig.12 Cross-sectional microstructures of the model bucket. (S.H.T:Solution Heat Treatment)

Fig.13 shows microstructure of the single crystal bucket after aging heat treatment in the position C. The precipitated  $\gamma'$  phases morphology of the model single crystal bucket is the same as the round bar specimen. Then, a difference of microstructure isn't observed in both specimens.

Generally, the bucket becomes thick compared with the round bar specimen. Therefore, the cooling speed after solution heat treatment becomes late and then precipitated  $\gamma'$  phases tends to become large in the bucket. Superalloy K has the excellent characteristic to be suitable for the heat treatment. At the model single crystal bucket, any coarsening of precipitated  $\gamma'$  phases isn't observed and also solution heat treatment was easily conducted as shown in fig. 12.

Next, a specimen with 4mm diameter was taken from the dubtail part of the blade and then creep rupture test was carried out. Fig. 14 shows creep rupture strength of the specimen that was cut down from the single crystal bucket. It is cleared that the bucket has the same creep rupture strength as the round bar specimen and that the decline of creep rupture strength doesn't occur.



(a) Round bar (b) Model bucket

Fig.13 SEM micrographs  $\gamma/\gamma'$  microstructure of the model bucket and round bar specimen after aging.

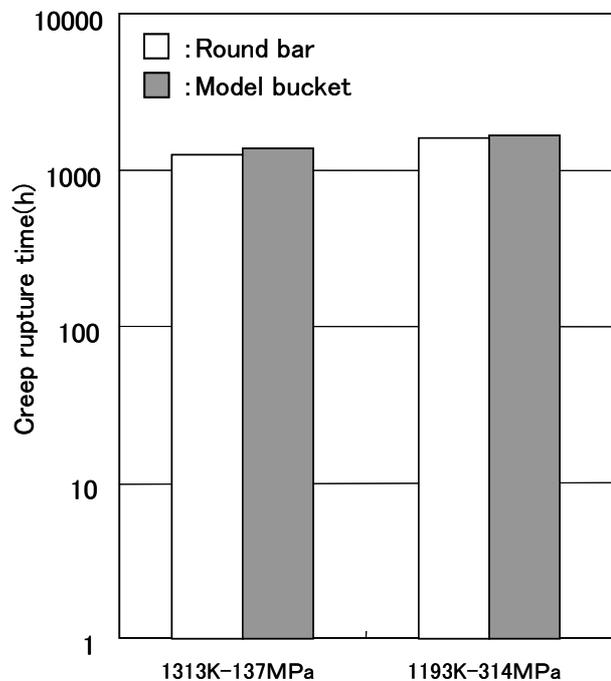


Fig.14 Creep rupture strength of the specimen that was cut down from the single crystal model bucket and round bar specimen.

## 5. Conclusions

Several kinds of superalloys with about 5mass% Re were designed in order to develop the 3rd generation single crystal superalloy for the power generation gas turbine bucket. In those superalloys, effects of alloy element on creep rupture strength, oxidation resistance, hot corrosion resistance and the single crystal castability are evaluated.

The single crystal superalloy designed in this research had more than 20 K higher temperature capability than the 2nd generation single crystal superalloy. And designed superalloy showed excellent hot corrosion resistance and good single crystal castability. However, the oxidation resistance of the designed superalloys was rather bad than the 2nd generation single crystal superalloy.

A lot of knowledge to improve oxidation resistance without reducing temperature capability was obtained in this work. The new single crystal alloys that have excellent creep strength, hot corrosion resistance and oxidation resistance have been developing based on this knowledge. The knowledge of this research can contribute to development of the 3rd generation single crystal superalloy of which the characteristic was more excellent.

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## References

K. Harris, G. L. Erickson, W. D. Brentnall, J. M. Aurrecochea, and K. G. Kubarych, 1992, "Development Of The Rhenium Containing Superalloys CMSX-4 and CM 186 LC For Single Crystal blade and Directionally Solidified Vane Applications in Advanced Turbine Engines," *Superalloys 1996*, pp. 297-306.

G. L. Erickson, 1996, "The Development and Application of CMSX-10," *Superalloys 1996*, pp. 35-44.

W. S. Walston, K. S. Ohara, E. W. Ross, T. M. Pollock and W. H. Murphy, 1996, "RENE N6: Third Generation Single Crystal Superalloy," *Superalloys 1996*, pp. 27-34.

Y. Koizumi, T. Kobayashi, T. Yokokawa, T. Kimura, M. Osawa, and H. Harada 1997, "Third Generation Single Crystal Superalloys with Excellent Processability and Phase Stability," *Materials for Advanced Power Engineering 1998*, pp. 1089-1098

J. C. Corman, 1995, "H Gas Turbine Combined Cycle Power Generations System for the Future," *International Gas Turbine Congress, 95-YOKOHAMA - IGTC-143*, pp. I - 267- I - 273.

J.S. Joyce, 1995, "The Prototype-Tested 3A-Series Gas Turbines," *International Gas Turbine Congress, 95-YOKOHAMA - IGTC-145*, pp. I - 283- I - 289.

R. Former, 1997, "Reliant Service-testing First 184-MW PG7251FB in Simple Cycle Operation," *Gas Turbine World: May-June 1992*, pp.10-14

N. Yukawa, M. Morinaga, Y. Murata, H. Ezaki, and S. Inoue, 1988, "High Performance Single Crystal Superalloys Developed by the d-electrons Concept," *Superalloys 1988*, pp. 225-234.

Y. Murata, S. Miyazaki, M. Morinaga, and R. Hashizume, 1996, "Hot Corrosion Resistant and High Strength Nickel-Based Single Crystal and Directionally-Solidified Superalloys Developed by the d-electrons Concept," *Superalloys 1996*, pp. 61-70.

K. Matsugi, Y. Murata, M. Morinaga, and N. Yukawa, 1992, "Realistic Advancement for Nickel-Based Single Crystal Superalloys by the d-electrons Concept," *Superalloys 1992*, pp. 307-316.

D. A. Ford, H. K. Bhangu, K. P. L. Fullagar, M. C. Thomas, P. S. Korinko, P. S. Burkholder, K. Harris, 1998, "Improved Performance CMSX4 Alloy Turbine Blades Utilizing PPM Levels of Lanthanum

and Yttrium," *Materials for Advanced Power Engineering 1998*, pp. 1035-1044

T. M. Pollock, W. H. Murphy, E. H. Goldman, D. L. Uram and J. S. Tu, 1992, "Grain Defect Formation During Directional Solidification of Nickel Base Single Crystals," *Superalloys 1992*, pp. 125-134.