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Development and Evaluation of High Strength Ni-base Single Crystal Superalloy,TMS-82+

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ABSTRACT

A new single crystal (SC) superalloy with a moderate Re addition (2.4wt%),TMS-82+, has been developed. TMS-82+ shows a higher creep rupture strength than the second and even the third generation single crystal superalloys. The composition of the alloy was designed to have a large negative lattice misfit with a computer aided alloy design program which was developed in National Institute for Materials Science (NIMS-ADP) . TMS-82+ had a stress rupture temperature advantage over 30 ℃ in comparison with the second generation SC superalloys on 137MPa/10^5hours. The large negative lattice misfit enhances formation of continuous γ' platelets which is called raft structure and fine interfacial dislocation networks during the creep tests, which are considered to disturb the movement of dislocations and increase creep strength. The other properties such as high temperature tensile strength, low cycle fatigue and oxidation resistance are equivalent to those of second generation SC superalloys. As a result of rainbow rotor test, there are no damage such as erosion, oxidation, creep and fatigue in TMS-82+ blade.

INTRODUCTION

The thermal efficiency of the gas turbine can be improved by increasing the turbine inlet gas temperature. To increase the turbine inlet gas temperature, the materials for turbine blades and nozzles are required to have higher temperature capability. Ni-base single crystal (SC) superalloys have higher creep strength in comparison with conventional and directionally solidified superalloys. So advanced gas turbine plant is adapting a Ni-base single crystal superalloy for blades and nozzles [Y.Ishida et.al. 2001].

Creep rupture strength of SC superalloys are reported to be improved by adding Re. Then, the second generation SC superalloys which contain 3% Re [A.D.Cetel et.al. 1998, G.L.Erickson et. al. 1994, W.S.Walston et.al. 1996], and the third generation SC superalloys which contain 5 to 6 % Re [W.S.Walston et.al. 1996, G.L.Erickson 1996, Y.Koizumi et.al. 1998] have been developed. On the other hand, it is also reported that excess adding of Re to the Ni-base superalloys tends to increase the sensitivity of Re-rich TCP phase precipitation[R.Darolia et.al. 1988, T.Hino et.al. 1998] which is known to reduce the creep rupture strength. It is reported that *CMSX*-10, which is third generation SC superalloy, precipitates TCP phase during the high temperature agings. The creep rupture strength becomes equivalent to that of second generation SC superalloy *CMSX*-4 after 20000 hours exposures at 982°C[G.L.Erickson 1996].

So, we intended to develop a new SC superalloy which has excellent phase stability and creep strength with a moderate amount of Re addition.

ALLOY DESIGN

Alloy design was conducted with the NIMS-ADP. This program can estimate material properties (creep rupture life, heat-treatment window, phase stability, concentrations of solid solution elements in γ and γ' phases, volume fraction of γ' phase, lattice misfit between γ and γ' phases etc.) by equations derived empirically from mechanical properties of SC superalloys [H.Harada et.al. 1988]. Schematic flow of this program is shown in Fig. 1.

The developed alloy was designed to have superior creep rupture strength by an effective use of negative lattice misfit ($a\gamma > a\gamma'$). The target of creep rupture life at 1100°C/137MPa was designed to have longer than 200h (e.g., 100h for *CMSX*-4). Re content was restricted to be less than 2.5%, which is designed to prevent precipitation of TCP phases and reduce the raw materials cost. The alloy density was set below 8.9g/cm^3 and the solution heat treatment window was designed to be larger than 50°C. Other properties such as long-term phase stability, corrosion/oxidation resistance and castabilty were also considered. The phase stability was estimated by a Solution Index (SI) value [H.Harada et.al. 1988]. SI values is defined as, SI = Σ (Ci/CLi), where Ci is an atomic fraction of i-th element in γ' phase and CLi is a solubility limit of i-th element in γ' phase of the Ni-Al-i-th element ternary system. If the SI value exceeds 1.25, precipitation of TCP phases is expected. After some calculations with NIMS-ADP and experimental screening test, we obtained TMS-82+. The alloy composition of TMS-82+ is shown in Table I with the other second and third generation SC superalloys.

Table I Typical chemical composition of tested and reference specimens.

mass%

Alloy	Co	Cr	Mo	W	Al	Ti	Ta	Hf	Re	Ni	SI
TMS-82+	**7.8**	**4.9**	**1.9**	**8.7**	**5.3**	**0.5**	**6.0**	**0.1**	**2.4**	**Bal.**	1.20
TMS-75	**12.0**	**3.0**	**2.0**	**6.0**	**6.0**	**-**	**6.0**	**0.1**	**5.0**	**Bal.**	1.10
***René* N5**	**7.5**	**7.0**	**1.5**	**5.0**	**6.2**	**-**	**6.5**	**0.15**	**3.0**	**Bal.**	-
***CMSX*-2**	**5.0**	**8.0**	**0.6**	**8.0**	**5.5**	**1.0**	**6.0**	**-**	**-**	**Bal.**	-
***CMSX*-4**	**9.0**	**6.5**	**0.6**	**6.0**	**5.6**	**1.0**	**6.5**	**0.1**	**3.0**	**Bal.**	-
***René* 80**	**9.5**	**14.0**	**4.0**	**4.0**	**3.0**	**5.0**	**-**	**-**	**-**	**Bal.**	-

*René80 is a equiaxial alloy and C0.07%,Zr0.04%,B0.016%are contained

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MATERIAL PROPERTIES OF TMS-82+

Microstructure and Heat-Treatment

Fig. 2 shows the microstructures of TMS-82+ in the as-cast condition and as-heated for 2 hour between 1280°C and 1360°C. Most of the γ' precipitates are dissolved into the γ phase at 1280°C but up to 1340°C, incipient melting is observed. TMS-82+, therefore, has a wide solution heat treatment window over 60°C, which means very good heat-treatment temperature capability. Fig. 3 shows the micrograph after the following heat treatment. Average edge dimension of cuboidal γ' phase is precipitated about 0.4-0.5 μm with regular alignment.

Solution heat-treatment : 1280-1300°C/1-2 hours→1300-1320°C/5hours→R.T. (A.C.or G.F.C.)
Aging heat-treatment : 1100°C/4hours→R.T. (A.C. or G.F.C.) + 780°C/20hours→R.T. (A.C. or G.F.C.)

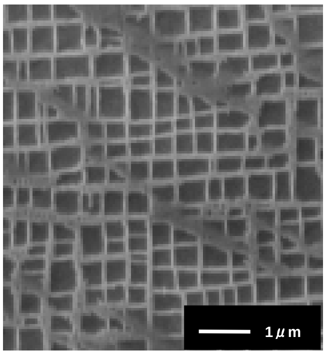

Fig.3 Micrograph at as-heat-treated condition.

Microstructural Stability

Fig. 4 shows TTT diagram of *CMSX*-10 cited from reference [G.L.Erickson 1994] and the aging test results of TMS-82+. Third generation SC superalloys which has high Re content exhibit greatest propensity for TCP phase formation with exposure at about 1090-1150ºC[5]. Re content of TMS-82+ was designed to be less than 2.5wt% to reduce propensity for TCP formation. So the reduction of creep strength due to the formation of TCP phase is not so high under high temperature and low stress condition.

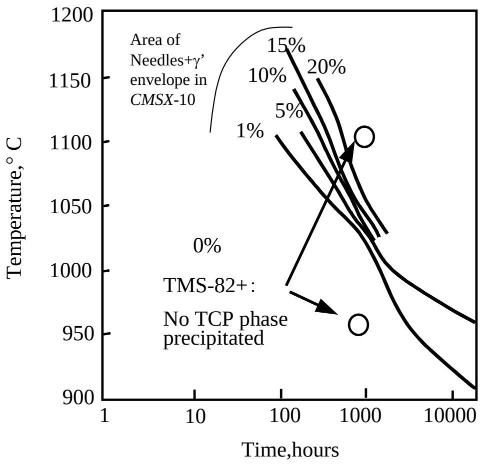

Fig. 4 TTT diagram of *CMSX*-10 and TMS-82+ .

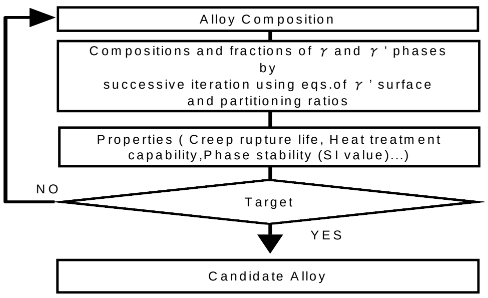

Fig.1 Schematic flow chart of NIMS Alloy Design Program.

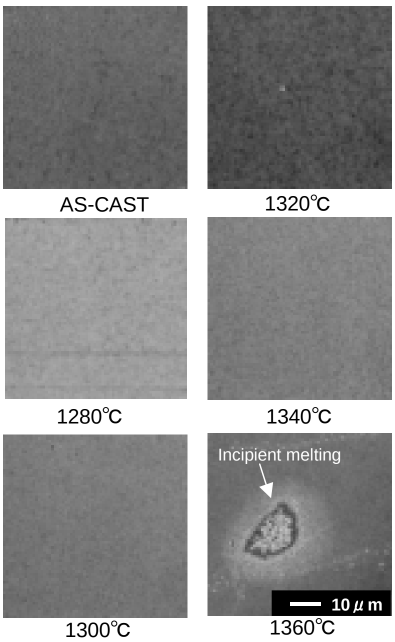

Fig.2 The result of solution heat-treatment trials at different temperature for 2 hours.

Creep Property

Fig. 5 shows the creep rupture curves of TMS-82+, with those of CMSX-4 [G.L.Erickson et.al. 1994], TMS-75 [Y.Koizumi et.al. 1998], RenéN5 [W.S.Walston et.al. 1996], RenéN6 [W.S.Walston et.al. 1996, K.S.Ohara et.al.] and MC-NG (MC544) [P.Caron 2000, D.Argence et.al. 2000]. MC-NG (MC544) is a fourth generation SC superalloy which contained Ru element.

The creep rupture strength of TMS-82+ is superior to those of the second generation SC superalloys such as *CMSX*-4 and *René*N5 in all the stress and temperature range, the temperature capability of TMS-82+ is 30°C higher than second generation SC superalloys at 137MPa. Moreover, in the higher temperature and lower stress range, TMS-82+ is stronger than the third generation SC superalloys such as TMS-75 and *René*N6, and fourth generation SC superalloy *MC-NG* (MC544).

Fig. 6 shows creep strain rate of TMS-82+ plotted against creep time under 1100°C/ 137MPa with the third generation SC superalloy TMS-75 . Creep strain rate of TMS-82+ is lower than that of TMS-75 on all the test time and TMS-82+ also has a long secondary creep area. Fig. 7 shows the raft structures and dislocation networks formed in TMS-75 and TMS-82+ at initial stage of secondary creep. The morphology of raft structure normal to the stress direction in TMS-82+ is more continuous and dislocation network spacing is finer than TMS-75 In creep condition, the raft structure and interfacial dislocation networks between γ and γ' phases are formed in Ni-base superalloys.

The raft structure improves the creep resistance effectively by providing effective barriers to dislocation climb around γ' platelets[R.A.Mackay et.al. 1984] and more continuous raft structure can disturb the dislocation movement effectively. Once the good rafted structure is established, dislocation climb becomes very difficult. In this condition dislocation cutting into γ' platelet is supposed to be the predominant creep mechanism. Finer dislocation network can act as a very effective barrier to this. This seems to be the reason TMS-82+ has good creep strength.

It is considered that the larger negative lattice misfit enhance to form the more continuous raft structure and finer dislocation network [H.Harada 1988]. Table. II shows the lattice misfit of TMS-82+, TMS-75 and *CMSX*-4 measured at 1100°C by X-ray diffraction techniques. The lattice misfit of TMS-82+ is negative and the absolute value is larger than that of TMS-75. It is considered the reason TMS-82+ has more continuous raft structure and fine dislocation network. The lattice misfit of TMS-82+ is more negative than *CMSX*-4. It is also considered the raft structure of TMS-82+ is more continuous and interfacial dislocation network is finer than that of *CMSX*-4. This seems the creep strength of TMS-82+ has higher than that of *CMSX*-4.

<u>Tensile Properties</u>

Fig. 8 shows the high temperature strengths of TMS-82+ and *CMSX*-4[C.K.Bullough et.al. 1998]. Yield strength and ultimate tensile strength of TMS-82+ are as same as that of *CMSX*-4. Tensile properties of TMS-82+ seems to be equivalent to that of second generation SC superalloy.

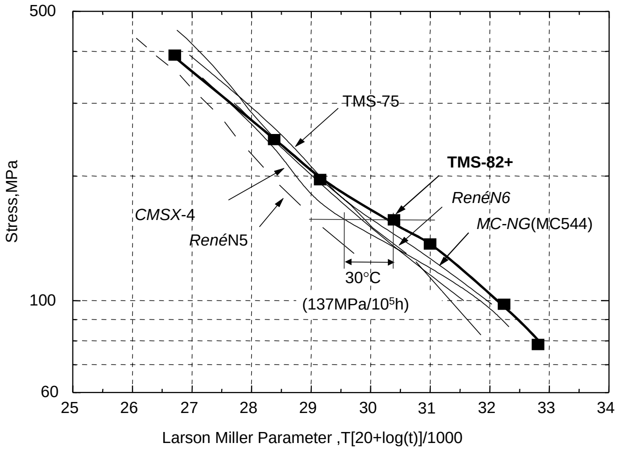

Fig 5 Creep rupture strengths of TMS-82+, *René*N5, *CMSX*-4, *René*N6,TMS-75 and *MC-NG* (MC544).

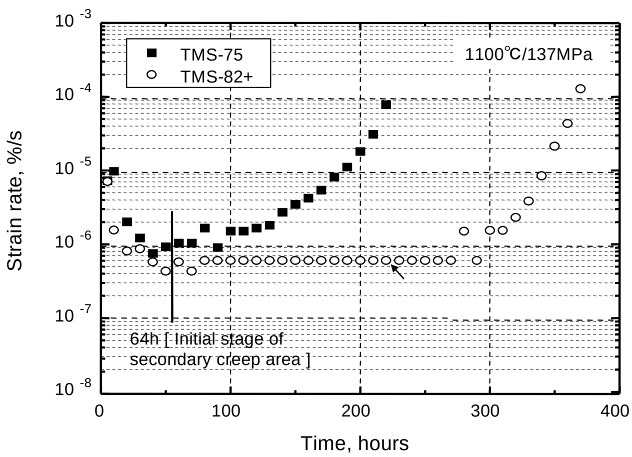

Fig. 6 Creep strain rate of TMS-82+ and TMS-75 paralell to the [001] direction plotted against time at 1100°C/137MPa.

<u>Low Cycle Fatigue Properties</u>

Fig. 9 shows the low cycle fatigue properties of TMS-82+ and *CMSX*-4[The society of Materials Science 2001]. Solid line shows low cycle fatigue lives under compression hold (C-H) wave condition at 900°C and 1000°C. Broken line shows low cycle fatigue lives at 900°C under no hold triangular wave condition (N-H). Low cycle fatigue lives of TMS-82+ is almost the same as that of *CMSX*-4. This shows low cycle fatigue property of TMS-82+ is equivalent to that of second generation SC superalloys.

In addition to this, low cycle fatigue life of TMS-82+ with compression hold was almost same as that of without compression hold at 900°C. Low cycle fatigue life of Ni-base superalloys are decreased under compression hold condition [R.Viswanathan 1989]. This shows TMS-82+ has good low cycle fatigue resistance in compression hold condition in comparison with the other second generation SC superalloys.

Table II : Lattice misfit of TMS-82+,TMS-75 and *CMSX*-4.

	TMS-82+	TMS-75	*CMSX*-4
Lattice Misfit (1100°C)	-0.24	-0.17	-0.13

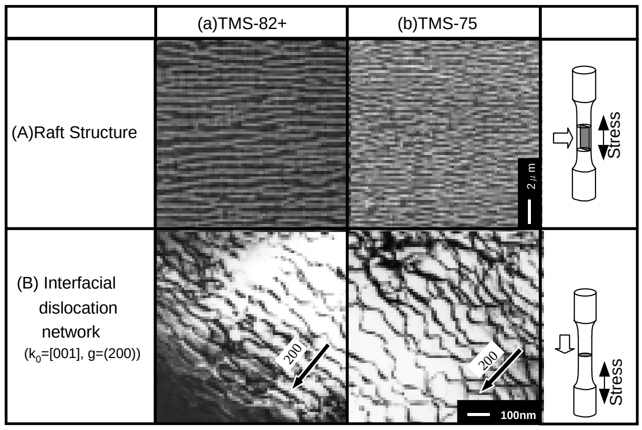

Fig..7 Raft structure (A) and dislocation network on γ/γ'interface(B) in TMS-82+ (a)and TMS-75(b); creep interrupted at 64 hours under 1100°C/137MPa.

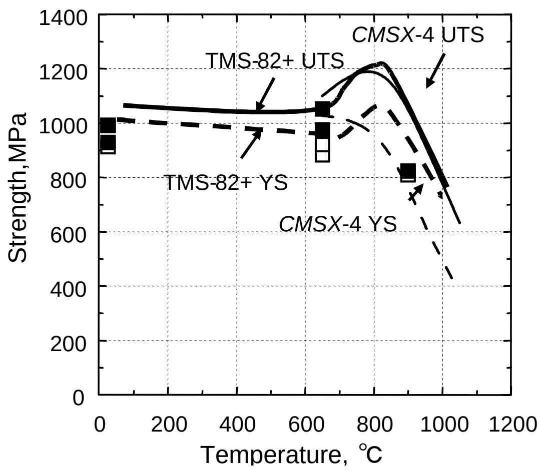

Fig.8 Tensile strengths of TMS-82+ and *CMSX*-4 parallel to the [001] direction.

Oxidation Resistance

Fig.10 shows weight gains of TMS-82+, *René*80 and *CMSX*-4 through an isothermal oxidation test and cross section micrographs of TMS-82+ and *René*80 at 950°C for 1000 hours. Weight gain of TMS-82+ is much smaller than that of *René*80 and equivalent to *CMSX*-4. Oxidized area of TMS-82+ is also much thinner than that of *René*80. These results shows that TMS-82+ has a good oxidation resistance.

RAINBOW ROTOR TEST

For final evaluation of TMS-82+ alloy, 15MW gas turbine blades were made and rotating test (rainbow rotor test) had been conducted in an actual turbine. The condition of rainbow rotor test is shown as below.

Inlet gas temperature	: 1345°C
Operation pattern	: Daily-start- stop
Number of start-stop	: 55 cycles
Total operation time	: 430 hours
Fuel	: kerosene

Fig.11 shows the blade after service. No damages such as oxidation, erosion, fatigue cracking and creep deformation were observed in the visual inspection.

Destructive investigation was conducted as shown in Fig.12. The blade was cut perpendicular and parallel to the longitudinal directions of the airfoil and metallurgical evaluations were conducted.

Fig.13 shows the microstructure of blade before service. Homogeneous distribution of cuboidal γ' precipitates with 0.4-0.5 μm diameter were observed. The harmful phases, such as σ and η phase, were not observed.

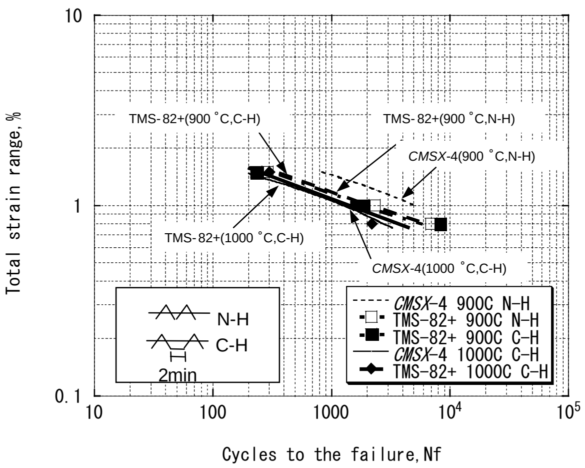

Figure9: Low cycle fatigue lives of TMS-82+ and *CMSX*-4 parallel to the [001] direction.

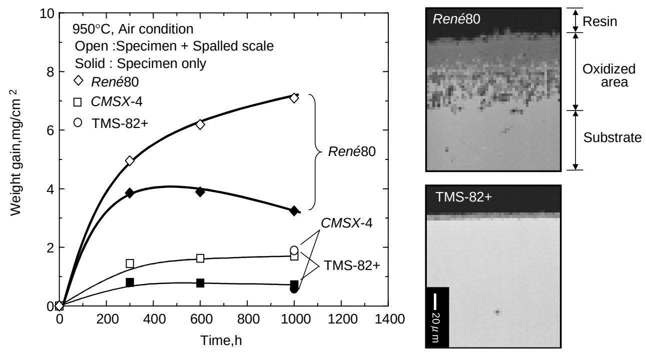

Fig. 10 Weight gains of TMS-82+, *René*80 and *CMSX*-4 and cross section micrographs of TMS-82+ and *René*80 during oxidation test at 950°C for 1000 hours.

The micrographs of the perpendicular and parallel sections to the longitudinal direction of the blade are shown in Fig.14 and Fig.15, respectively. The size of γ' phase was increased in leading edge section, however σ and η phase phases were not observed. Fig.16 shows cross section micrograph near the surface. Thick oxide layer was not observed.

The alloy composition of TMS-82+ was designed to strengthen by formation of raft structure. However, there was not shown the formation of raft structure. *CMSX*-2 blade serviced about 500 hours in same gas turbine was formed raft structure near the surface of the airfoil [Y. Yoshioka et.al. 2002].

The lattice misfit between γ and γ' of *CMSX*-2 and TMS-82+ at room temperature calculated by NIMS-ADP is shown in Table III. The lattice misfit of *CMSX*-2 is larger than that of TMS-82+. This seems that TMS-82+ tends to form the raft structure in comparison with *CMSX*-2. However TMS-82+ is contained Re element. Re tends to be segregated at γ / γ' interface and play a role in retarding the coarsening of γ' precipitates [H. Murakami et.al. 1995]. It is considered the reason the raft structure was not formed in TMS-82+.

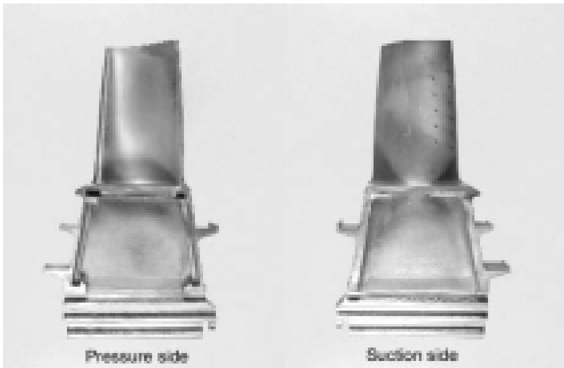

Fig.11 15MW gas turbine after service

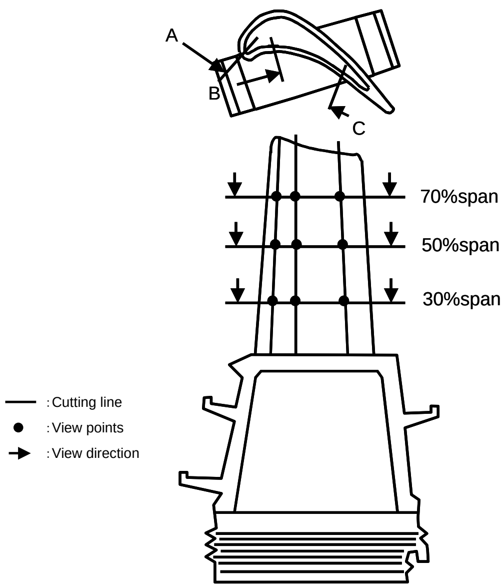

Fig.12 Sampling location of tested gas turbine blade

Table III : Lattice misfit of TMS-82+ and *CMSX*-2

	TMS-82+	*CMSX*-2
Lattice Misfit（RT）	0.181	0.294

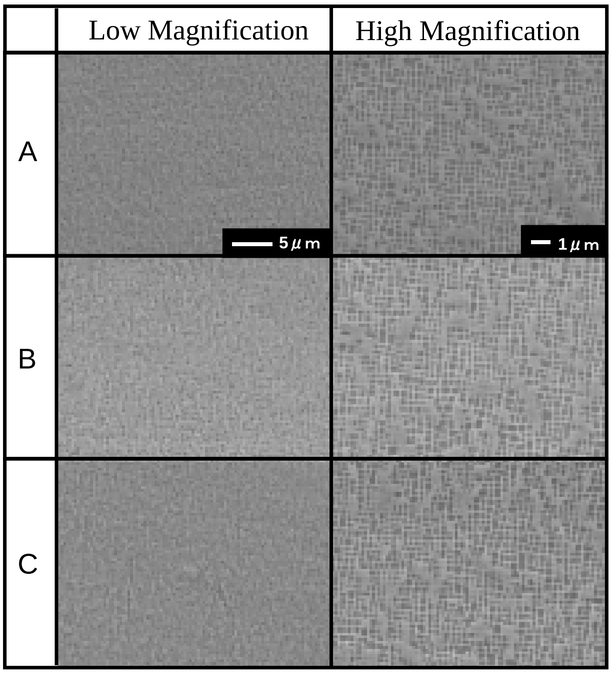

Fig.13 Cross-section micrograph of 50%span before service.

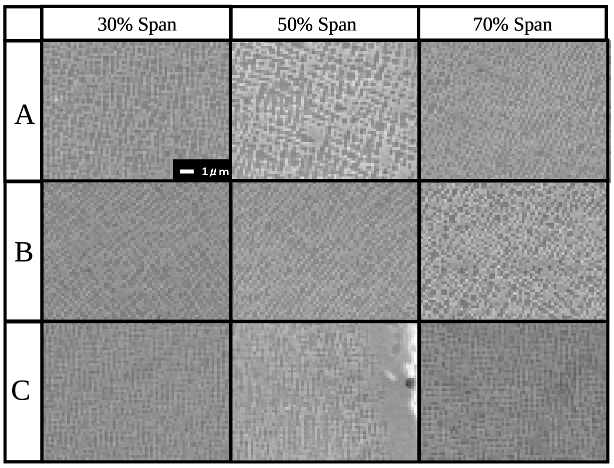

Fig.14 Cross-section micrograph of TMS-82+ serviced blade perpendicular to longitudinal blade direction.

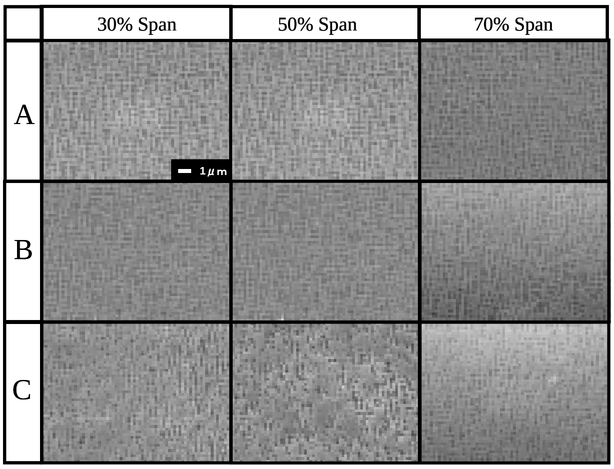

Fig.15 Cross-section micrograph of TMS-82+ serviced blade parallel to longitudinal blade direction.

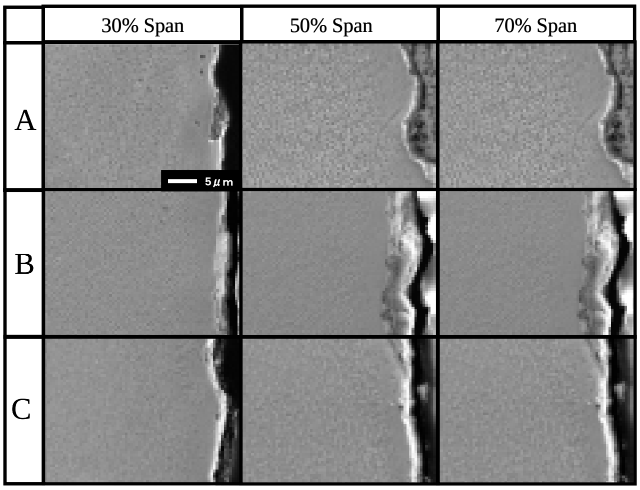

Fig.16 Cross-section micrograph of TMS-82+ serviced blade perpendicular to longitudinal blade direction.

CONCLUSIONS

In this study, we developed a new SC superalloy having excellent creep properties in comparison with present second generation SC superalloys. The following results were obtained.

1. We developed a new SC superalloy,TMS-82+ aided by the NIMS-ADP. The creep strength of the developed alloy is higher than those of second generation SC superalloys and even higher than third generation SC superalloys at high temperature and low stress condition.

2. In microstructural observation, the morphology of raft structure normal to the stress direction in TMS-82+ is more continuous and dislocation network spacing is finer than the third generation SC superalloy TMS-75. These are considered to the reasons for the creep property of TMS-82+ being superior to that of other SC superalloys especially in high temperature and low stress condition.

3. TMS-82+ has good high temperature tensile strength, low cycle fatigue strength and oxidation resistance equivalent to those of *CMSX*-4 with excellent phase stability.

4. As a result of rainbow rotor test, there are not any damages such as oxidation, erosion, fatigue cracking and creep deformation. From destructive observation, there are not shown excess size of γ' phase. Harmful phases, such as σ and η phase, were also not precipitated.

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