

NRIM SR-92-01

Design and Development of Ni-base Superalloy and Ti Alloys

by

Michio YAMAZAKI

NRIM Special Report
(Research Report)

No. 92-01

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National Research Institute for Metals
2-3-12 Nakameguro, Meguro-ku, Tokyo, Japan

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Abstract

This overview article describes what have been done in NRIM for design and development of Ni base superalloys and Ti alloys of high temperature use. Most of those works were performed in two national projects. For Ni base alloys we have developed alloy design programs in which compositions of two phases, γ and γ' , can be estimated and properties of alloys are described and predicted as functions of the phase compositions and the phase volume fraction. For Ti alloys similar design programs were studied for α and β phases, and later for α and α_2 phases. For Ni-base alloys, after developing the first version of the design program, we applied this to develop conventionally cast alloys, directionally solidified columnar alloys, single crystal alloys, superplastically workable alloys, and oxide dispersion strengthened alloys. The second version of alloy design program for Ni-base alloys was then developed and was chiefly applied to single crystal alloys. For the above alloy developmental projects we have proposed a number of new alloys. By using the alloys proposed by us, process studies were done mainly by companies participating in the projects.

Keywords: *Ni-base superalloy, Ti alloy, Superplasticity, ODS alloy, Single crystal alloy, DS alloy, Alloy design*

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1. INTRODUCTION

Ni-base superalloys and Ti alloys are the most important materials for gas turbine and jet engine hot section applications. Though extensive studies on ceramics and intermetallics have been done, Ni-base superalloys are still important materials and this situation is not considered to change in near future.¹⁾ The similar conclusion may be true for Ti alloys for compressor hot section applications.

Agency of Industrial Science and Technology (AIST) of Ministry of International Trade and Industry (MITI) planned and sponsored two national projects in which various types of nickel-base superalloys and Ti alloys were developed.

“Advanced Gas Turbine” was the first one and its main theme was of course the development of new gas turbines. Besides this main theme this project dealt with, from 1978 to 1985, developments of conventionally cast Ni-base superalloys (CC alloys) and directionally solidified columnar Ni-base superalloys (DS alloys),²⁾ to which we contributed. “Advanced Alloys with Controlled Crystalline Structures” was the second project.^{3),4)} The basic concept of the project resides in the understanding that properties of alloys depend on their microscopic crystalline structures as well as on their compositions, and hence controlling the former is very important and it can be an interesting research theme. Under this concept there would be many alloys to be studied, but due to

the restriction of the budget available, high temperature materials for gas turbines or jet engines were selected. Three types of nickel-base superalloys were chosen; they are single crystal alloys (SC alloys), superplastically forgeable P/M alloys, and oxide dispersion strengthened alloys (ODS alloys). In this project, Ti alloys, being superplastic as well as strong, were also developed. All those alloys require sophisticated manufacturing processes as well as compositions suitable for each of the processes. This second project was carried out from October 1981 to March 1989.

Our objectives in the both projects were to increase temperature capabilities of blade materials (CC, DS, SC, and ODS Ni-base alloys) and strengths of disk materials (superplastic Ni-base and Ti alloys) for gas turbines or jet engines. Titanium alloys were intended to be applied to compressor disks of the turbine, which usually are heated up to about 500 to 700 K by compressed air. The establishment of manufacturing processes for hollow air-cooled blades and for superplastically forged disks was also our target, but by using alloys to be developed by the projects.

There were no quantitative targets for alloy developments in the first project (Advanced Gas Turbine). In this project, the first turbine was designed by using commercial alloys for its blade materials; alloys Mar-M247 and Mar-M247 (DS) (**Table 1**) for CC and DS casting processes, respectively, were employed. Our targets were then to develop alloys superior to those for each process, respectively. Successful new

Table 1. Compositions of some representative Ni-base alloys, developed and commercial (mass %).

	Alloy	Type	Cr	Co	Mo	W	Ta	Al	Ti	C	B	Zr	Others
Developed	TM-321	CC	8.1	8.2	—	12.6	4.7	5.0	0.8	0.11	0.01	0.05	0.9Hf
	TM-269	CC	9.7	8.9	—	13.2	3.8	4.3	0.6	0.11	0.01	0.05	0.8Hf
	TMD-5	DS	5.8	9.5	—	13.7	3.3	4.6	0.9	0.07	0.015	0.015	1.4Hf
	TMS-12	SC	6.6	—	—	12.8	7.7	5.2	—	—	—	—	—
	TMS-62	SC	7.9	—	6.9	—	—	5.8	0.9	—	—	—	—
	TMO-2	ODS	5.9	9.7	2.0	12.4	4.7	4.2	0.8	0.05	0.01	0.05	1.1Y ₂ O ₃
Commercial	Mar-M247	CC	8.4	10.0	0.7	10.0	3.05	5.5	1.05	0.15	0.015	0.05	1.4Hf
	Mar-M247 (DS)	DS	8.0	9.5	—	9.5	3.0	5.6	0.8	0.07	0.015	0.015	1.4Hf
	PWA1480	SC	10.0	5.0	—	4.0	12.0	5.0	1.5	—	—	—	—
	MA6000	ODS	15.0	—	2.0	4.0	2.0	4.5	2.5	0.05	0.01	0.15	1.1Y ₂ O ₃

CC: Conventionally cast alloy, DS: Directionally solidified columnar alloy, SC: Single crystal, alloy, and ODS: Oxide dispersion strengthened alloy.

alloys to be developed were intended to be tested in the second gas turbine designed in the project. At present DS blades are not commercially used for land-based gas turbines, because DS blades of large sizes such as 150 mm in length are difficult to be cast. The turbine designed in this project was a high-pressure one which was then small in its size and hence small blades such as 70 mm in length were used. This situation lead us to development of DS blades.

For the second project (Advanced Alloys), some officials of AIST had decided targets before the project started. They set the targets, in principle, exceeding by appropriate degrees, for instance 10%, the properties of the commerical alloys of each type which were considered to be the best at that time. The details of the targets will be described later for each type of alloys.

The present author and his colleague of National Research Institute for Metals (NRIM) designed alloys having properties satisfying, desirably, the targets and being suitable for each process. They were proposed as candidate alloys for process studies, which were chiefly carried out by private companies participating in the two projects. More specifically, those companies performed their works as members of the organizations established for the projects, i.e. "Engineering Research Association for Advanced Gas Turbines" for the first project and "Research and Development Institute of Metals and Composites for Future Industries" for the second. Two other national research institutes participated in the second projects.

Process studies mentioned here were not the ones to figure out new types of processes but rather ones in which various factors for manufacturing parts by using proposed alloys were optimized. This point will be discussed more in detail in section 2.2.

In this overview I will first describe a general consideration on the alloy design or materials design.

Next, after giving the basic knowledge for Ni-base superalloys, I will explain our alloy design techniques and alloy developmental activities done in the above described two national projects and our own themes after the projects. Besides the alloy developments performed by NRIM I will also refer to studies

concerning process optimizations done by other national research institutes and the companies participating in the above two projects, the emphases being put on the former (alloy developments, especially for Ni-base superalloys).

2. A GENERAL ASPECTS OF MATERIALS DESIGN

2.1. Sequences of Materials Design

The ideal sequence of materials or alloy design is:

- (1) Required properties
- (2) Predicted alloy microstructures
- (3) Predicted alloy compositions and processes

That is, for any required property, we should first predict the alloy microstructure that can satisfy the property. For the term "alloy microstructure" I here propose to grant it more general than usual; I include compositions of each phases or microscopic constituents as well as general meaning of microstructures such as grain sizes, textures, dislocation densities and others. Then we must give the alloy composition and the process to realize the predicted alloy microstructure above. A direct mode of this sequence is obviously quite difficult. This difficulty would be understood by pointing out that one should also indicate nonexistence of (2) or (3) above for an excessive requirement set in (1).

The compromise sequence is as follows:

- (a) Given alloy compositions and processes
- (b) Predicted alloy microstructures
- (c) Predicted properties

In principle, when the alloy composition and the process for it are given the alloy microstructure is fixed exclusively. The prediction of the microstructure is possible though it is not so easy. Our final purpose is not the prediction of the microstructure but that of the prpoerties from the predicted microstructure. This step, (b) to (c) is much more difficult than the step, (a) to (b). For the overall sequence from (a) to (c) we must rely much more upon experimental facts or experimental equations than upon theories or theoretical models. Once a computer model for the sequence of (a) to (b) is accomplished, of course realized only for limited composition ranges at present, we can do the former sequence (1) to (3) by the

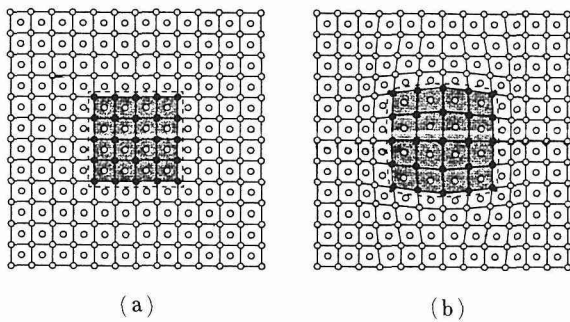


Fig. 3 Precipitation of γ' phase (within the dotted line frames) from γ phase, seen on $\{100\}$ plane.
 (a): Coherent precipitation without lattice mismatch.
 (b): Coherent precipitation with lattice mismatch.

Alloys designed to have high γ' phase volume fractions as 50 to 70% (at room temperature or alloy use temperatures such as 1050 K) have high strengths at elevated temperatures. They are, however, very hard to be forged from ingots, so casting or P/M procedures are employed for high γ' alloys.

Fig. 4 shows three casting procedures for making turbine blades. Cores are used to make air-cooled blades but are not shown in this figure. **Photo. 1**

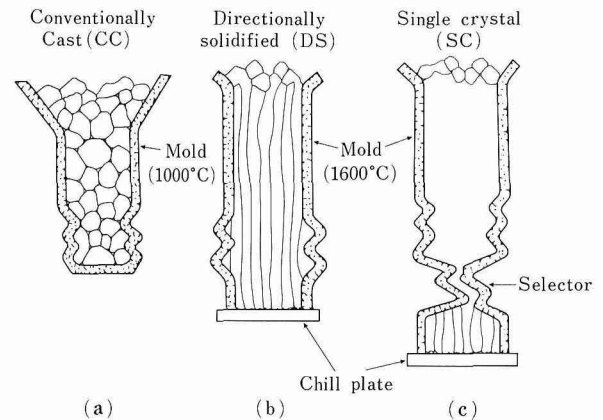


Fig. 4 Illustration of three processes for cast turbine blades: (a): CC, (b): DS, and (c): SC.

indicates air-cooled turbine blades made by three casting processes shown in Fig. 4.

3.2 Conventional Casting (CC)

Conventional casting (CC) results in polycrystalline materials. Equiaxed structures are favorable for CC casting, but sometime unfavorably directed columnar structures are produced in which boundaries of columnar crystals are perpendicular to the applied stress. Casting variables and probably alloy composi-

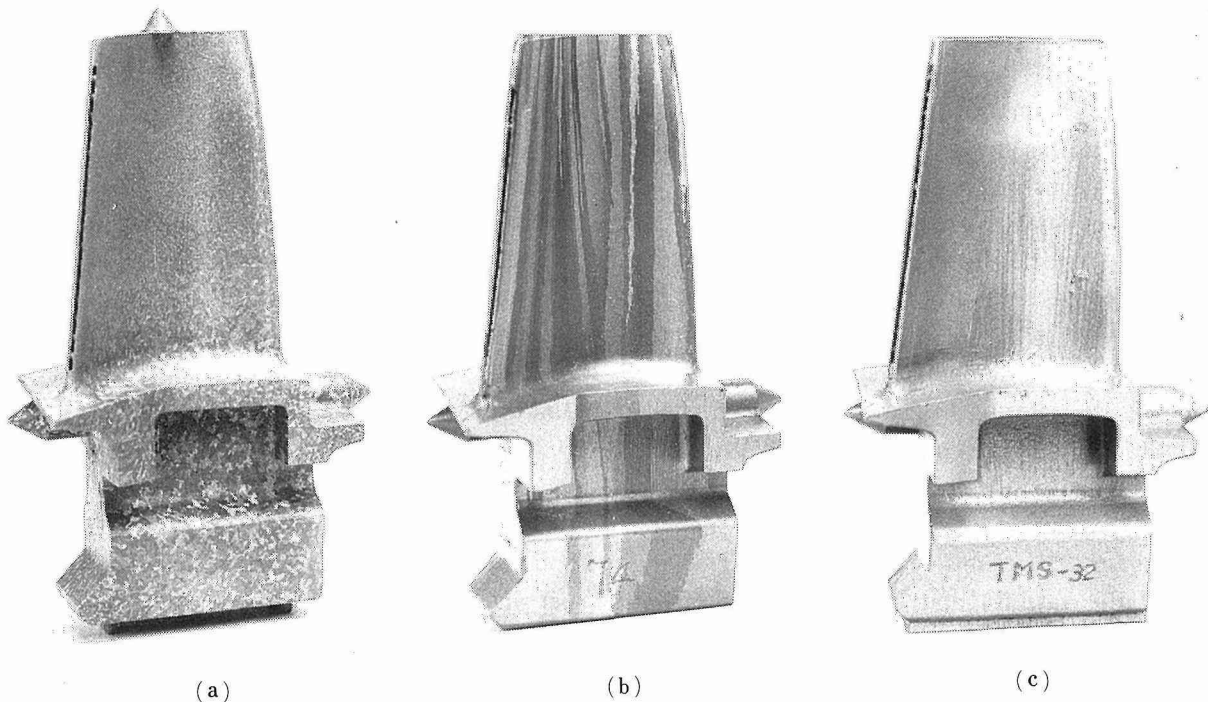


Photo. 1 CC blade (a), DS blade (b), and SC blade (c), the lengths being about 9 cm. All air-cooled hollow blades made using alloys developed by NRIM; cast by Komatsu-Howmet, Ltd. (CC) and IHI (DS and SC).

tions may affect the formation of favorable equiaxed structure.

3.3 Directional solidification (DS)

Directional solidification (DS) casting is applied to avoid grain boundaries perpendicular to the applied stress. Grain boundaries are known to be weak at high temperatures and in spite of various efforts there have not been effective means to improve their strengths comparable to those for matrices which can be strengthened, in the case of Ni-base superalloys, by designing alloys with higher γ' volume fractions and appropriate alloying of γ and γ' phases. In Fig. 4(b), a mold on a chill plate is heated above the melting temperature of the alloy to be cast and when the molten alloy is poured into the mold it holds the alloy in molten state except near the chill plate. Then the mold is gradually pulled down from the furnace which is heating the mold. The rate is, for instance, 50 mm/h. Columnar crystals from the chill plate start to grow until they fill the mold.

In producing air-cooled hollow blade by DS process described above, as shown in Photo. 1(b), a ceramic core is set in the mold. During cooling after DS solidification stress is yielded by the core onto the metal part and this stress causes cracking to the DS columnar metal part along the crystal boundaries. This is considered to occur at fairly high temperatures because (grain) boundaries are weak at high temperatures. To avoid this cracking we must consider about alloy compositions and casting processes.

3.4 Single Crystal (SC)

For single crystal casting, Fig. 4(c), we put a selector between the portion adjacent to the chill plate (called starter) and the main portion of the mold. One of the columnar crystals in the starter is selected by the selector to grow further as a single crystal into the main portion of the mold. Avoidance of (grain) boundaries itself is of course the merit of SC castings. More important are release of the alloying limitations for DS castings described above (cracking just after the casting) and applicability of higher solution temperatures (hence higher γ' volume fractions) due to elimination of C and B additions which are necessary for grain boundary strengthening for CC and DS casting alloys.

The orientations of columnar crystals growing from a chill plate are mostly [100] and consequently this is the single crystal orientation. Fortunately this orientation is the most favorable one in point of creep strength. However, some considerations will be required for keeping single crystals exactly in the [100] direction.

For design and development of single crystal alloys, besides their creep strengths we must consider other factors such as ductility, price, solution treatment windows (temperature difference between solvus and solidus, i.e. solution treatment temperature range), density, hot salt corrosion resistance, easiness of control of crystal direction, susceptibility to recrystallization during solution treatment. Controlling all of them by alloy design beforehand is difficult and hence some of them are simply evaluated after making specimens.

3.5 Oxide Dispersion Strengthened Alloys (ODS)

Introduction of fine oxide particles in γ' -strengthened alloys can be achieved by mechanical alloying in an attritor (See Fig. 5). Powders thus obtained are sealed in a capsule or a can and extruded at elevated temperatures. As extruded bars have fine grains and weak even they contain dispersoids. Grain coarsening is required. In this case, however, equiaxed structures give poor creep rupture strengths due to premature grain boundary cracking. To avoid this, like in the DS process, zone annealing is applied to the bars to give them elongated grains; aspect ratios being preferably more than 10. This zone annealing process is very sensitive one; the results depend on various factors. One of them is isothermal forging of the extruded bars to give them appropriate shapes as blades.

3.6 Superplastic Forging

Atomized powders of superalloys are, after sintering, superplastically or isothermally forged to give them appropriate shapes (turbine discs for instance) and also plastic deformation itself. For obtaining near net shapes we must use superplastic deformation. To get a big size preform for superplastic forging, we should avoid the usage of an extrusion machine, since it must be a huge one and is not economical. It means we must make fine-grained preforms to be forged

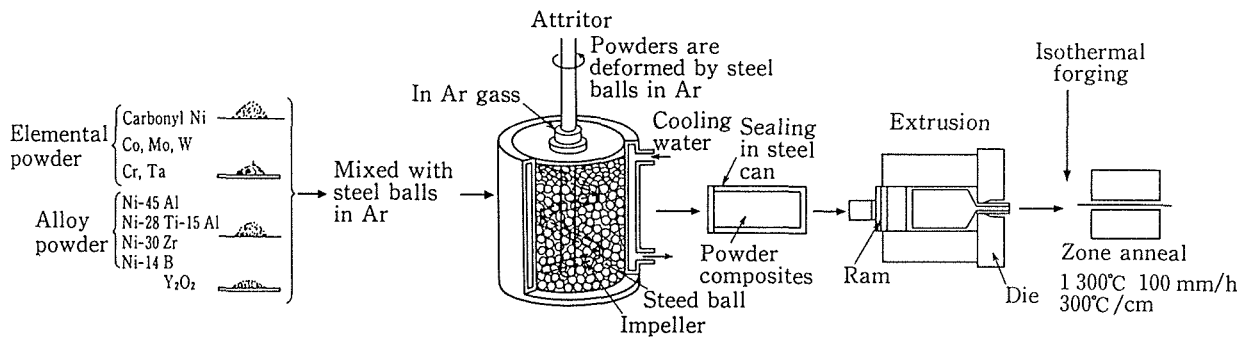


Fig. 5 Manufacturing process for ODS Ni-base superalloys.

superplastically only by atomization and sintering; this has been a fairly big research theme.

4. ALLOY DESIGN FOR Ni-BASE ALLOYS

All the Ni-base superalloys treated in the above-mentioned projects were high γ' content two phase alloys. The present author and his collaborators developed a computer-aided alloy design method for γ/γ' type nickel-base alloys.^{5),6)} The essential part of these alloy design programs is made up of giving pairs of γ and γ' phase compositions in multi-component systems.

Fig. 6 shows fundamental steps of the alloy design program described above. The left column of the figure shows the main flow of the program and the right some preliminary analyses or experiments to get necessary parameters or equations. Some remarks for Fig. 6 will be given bellow.

Steps A-1 and A-2

We start by assuming arbitrary γ' compositions which can equilibrate with γ phases. To do this we make the γ' surface equation (Work B-1 of Fig. 1). The γ' surface is the one of the γ' region of multi-component system, each point on the surface being connected by a tie line with a corresponding γ phase. The γ' surface is formulated by expressing Al concentration as a function of concentrations of other elements except Ni in the phase.

Step A-3

Solution index, SI, is explained by the following example. Solubility limits of Cr and W, for example, in Ni_3Al (basic γ' phase) are 14.0 and 5.8 atomic %, respectively. If we design a γ' composition of 8 and 3 atomic % for the two elements, respectively, (Al % is

determined as a function of the Cr and W concentrations according to γ' surface equation described above and Ni % is the balance), then

$$\text{Solution index} = (8/14.0) + (3/5.8) = 1.09$$

Standing on a simple principle, one should expect the maximum index value to be unity, fortunately, however, values slightly exceeding unity is possible and since we need maximum solid solution hardening in γ' we should utilize maximum SI values.

Steps A-6 and A-11

Those are preliminary rejection of dilute alloys, which are low in lattice parameters. The value, 3.577, is in angstrom unit and is rather arbitrary; the particular value is an example.

Step A-7

Partitioning ratio of an element is defined as the ratio of the concentration in γ' to that in γ (in equilibrium with γ'), or vice versa. This ratio depends on the particular element concerned and also on γ' composition. We do a regression analysis to get an equation to give the ratio for an element as a function of γ' composition; in principle we thus get one regression equation for each element. Those expressions for the partitioning ratios are equivalent to those for tie lines.

Step A-12

Mismatch, as explained by Fig. 3, is the difference between the lattice parameters of γ' and γ phases. Mismatches generally should be kept as low as possible but sometimes especially for single crystal alloys certain non-zero small values are preferable.

Step A-15

Mol fraction of γ' phase, which is nearly equal to

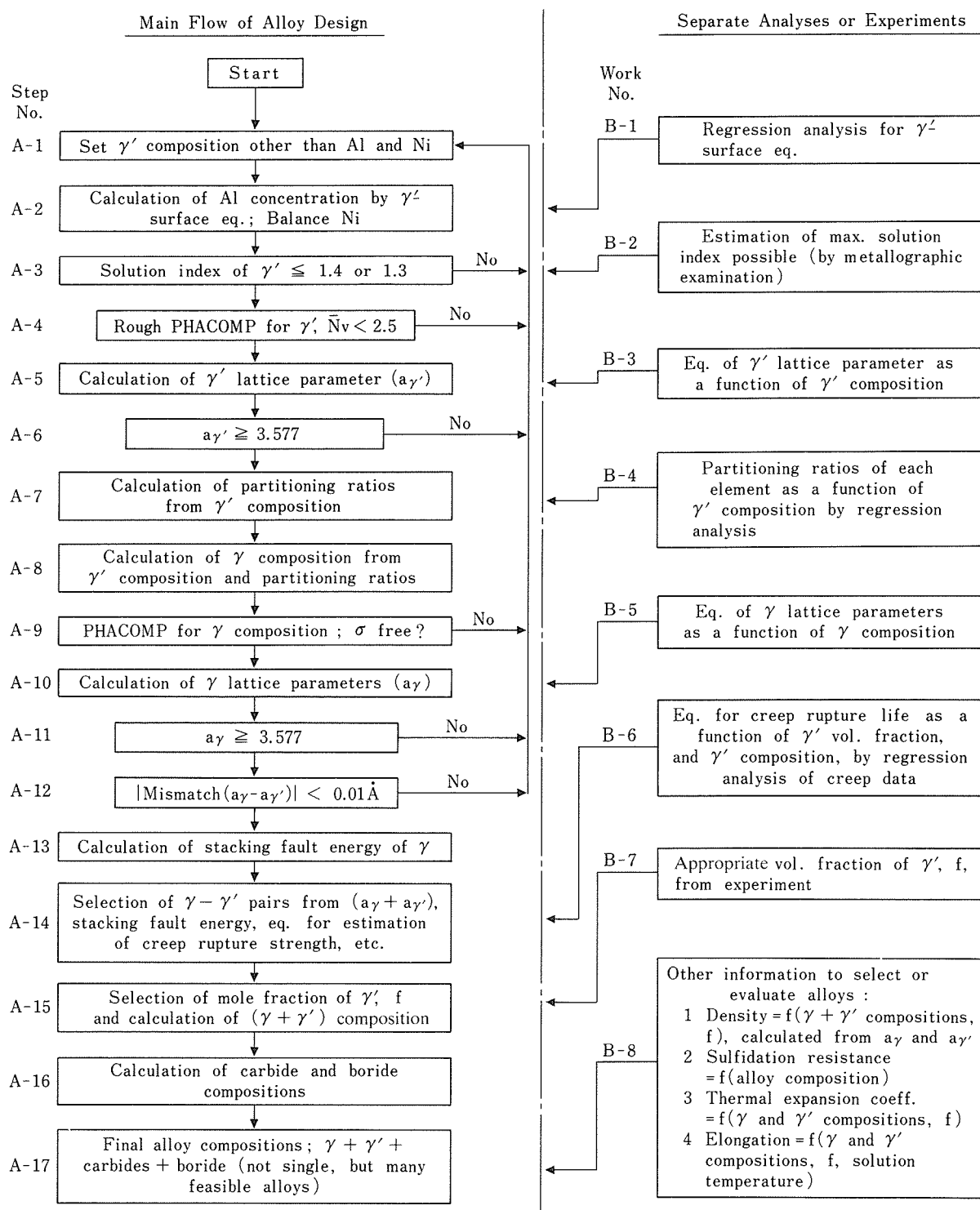


Fig. 6 Steps for alloy design program for Ni-base superalloys. The left column shows step-by-step main flow of alloy design and the right some analyses or preliminary experiments for the left. The sequence of this figure corresponds to 'Search program' of Fig. 7 and can be modified to 'Analyzing program' of Fig. 7.

the volume fraction, is one of the important factors in the Ni-base alloys, and appropriate designing fractions are determined by preliminary experiments. Most often utilized fractions are 0.6 to 0.75.

Step A-17

Other than γ and γ' phases, small amounts of carbides and borides are required for grain boundary strengthening except for SC alloys. Carbide and boride compositions are calculated as functions of particular sets of γ and γ' phases. Those are also given by some regression equations prepared by us.

Works B-6, B-7 and B-8

Various properties of alloys are estimated by regression equations. Important properties such as creep rupture lives are analysed as functions of γ' volume fraction as well as compositions of γ' phase.

We have essentially two versions of the alloy design program. The first one⁵⁾ depended on data of γ and γ' phase compositions determined by chemical analyses of electrochemically extracted γ' phases. Those analyses are not so accurate, so we measured γ and γ' phase compositions by EPMA analyses on samples with coarsened γ and γ' phases, and utilized them in the second version.⁶⁾ The second version was further improved by incorporating the effect of temperature on equilibrium compositions of γ and γ' phases.⁷⁾ So far only for SC alloys has been applied the new second version.

From other point of view, there are two types of alloy design programs for both of the two versions above. The first one is to give properties for a given alloy composition (Analyzing program, Left side of Fig. 7) and the second is to search compositions for desired properties (Search program, Right side of Fig. 7).

Besides the above described two versions and two types, there are also some minor modifications for the alloy design programs; they are, for instance, some improvements in regression equations for property estimation.

The alloy design programs mentioned above are not such that they can give the only one best alloy. The programs rather indicate some feasible alloys that are well worth being tested experimentally.

The above described design programs basically depend on analyzed phase compositions of many alloys. We have done somewhat more fundamental approaches to calculate phase compositions of γ and γ' phases for ternary systems using Cluster Variation Method (CVM)⁸⁾ We are further extending this to higher order multi-component Ni-base systems.⁹⁾ Those CVM methods, however, have not been used for alloy design jobs in the projects.

Fig. 8 shows an output of 'Search program' above for the developed single crystal alloy TMS-12, and in Table 2 are shown parameters appearing in Fig. 8.

To help understand this section, alloy design, Fig. 9 will be explained. This shows Ni corner of Ni-Al-A-B system; A and B being arbitrary additive elements. On the Ni-Al axis there is Ni_3Al , which has some solubility range and when elements A and B added there appears the γ' -region shown in the figure. The interface between the γ' -region and the $\gamma+\gamma'$ region we can define γ' -surface. Near Ni corner we have the γ -region and the γ -surface as well. On the γ' -surface we can see line 12-13 on which there are γ' compositions with SI (Solution index defined above) of 0.5 and line 7-8 on which γ' compositions of SI=1. It was found that SI can be somewhat larger than unity, which is shown by a bow 7-8. Line 9-10 is one of tie-lines between γ' surface and γ surface. Point 9 is a γ' having SI larger than unity. Partitioning ratios of each element between γ' and γ are functions of γ' composition and this corresponds to that each tieline, its direction and end point such as point 10, are functions of γ' composition on the γ' surface. For each tieline, such as line 9-10 we can design an alloy having an arbitrary γ' phase volume fraction such as point 11 (65% γ'). The γ' surface can be expressed by determined Al concentrations of γ' phases as a function of concentrations of A and B. This is called the γ' -surface equation.

5. CONVENTIONALLY CAST NI-BASE ALLOYS

Our objective was to develop alloys superior to alloy Mar-M247 (Table 1). Concentrations of elements effective to increase high temperature strengths, such as W and Ta, in gamma prime phases and hence in gamma phases, can be increased by

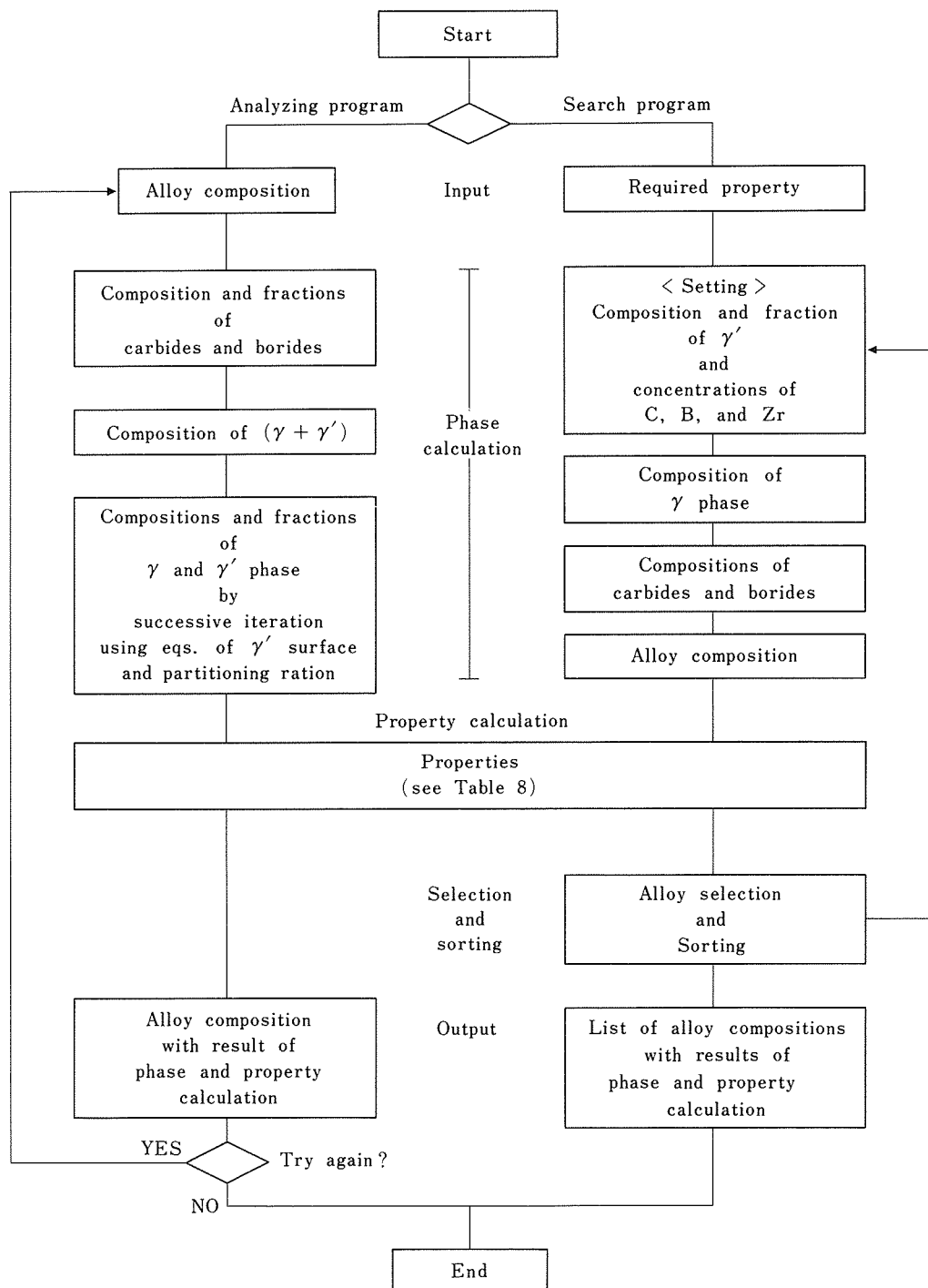


Fig. 7 Two types of practical application of alloy design based on Fig. 6. The left is to analyze properties of a given alloy and the right to find alloy composition for a given set of properties.

decreasing Cr concentrations. Cr is known to increase hot corrosion resistance. The balance between high temperature strengths and hot corrosion resistances can be changed with this adjustment between W plus

Ta and Cr. Thus many alloys with various gamma prime contents and various Cr concentrations in gamma-prime phase (and hence in gamma phase) were designed and examined experimentally.¹⁰⁾ As a

ALLOY TMS-12 ~~~~~ PHASE (AT 900°C) & PROPERTY CALCULATION ~~~~~											
	NI	CO	CR	MO	W	AL	TI	NB	TA	HF	RE
GP	72.89	0.00	2.09	0.00	3.04	18.06	0.00	0.00	3.92	0.00	0.00
G	72.56	0.00	16.74	0.00	6.38	3.45	0.00	0.00	0.87	0.00	0.00
ATPCT	72.76	0.00	8.01	0.00	4.39	12.16	0.00	0.00	2.68	0.00	0.00
WTPCT	67.70	0.00	6.60	0.00	12.80	5.20	0.00	0.00	7.70	0.00	0.00
F.GP	LAT.GP (A)		NV.GP	LIQ (C)		SOL2 (C)		H.COR.C		YS (MPA)	
0.596	3.594		2.325	1411.4		1359.8		287.31		598.1	
DENSITY	LAT.G (A)		NV.G	SOL1 (C)		SOLV (C)		H.COR.B		UTS (MPA)	
9.062	3.582		1.870	1396.3		1328.6		10.48		656.5	
SI	LM (%)	NV.G-NVC		RANGE (C)		WDW (C)		BB1	EL (%)	SPC.STRGTH	
1.173	0.327	0.197		15.1		31.1		0.00	4.7	15.689	
~~~~~ TRY AGAIN ? < YES (0), NO (1) > ~~~~~											

**Fig. 8** Output of 'Search program' of Fig. 7 for alloy TMS-12 as an example. Parameters in this figure are explained in Table 2.

**Table 2.** Parameters and properties appearing in the output of the alloy design program.

Character	Parameter or property	Condition
GP	Chemical composition of $\gamma'$ (at%)	900°C
G	Chemical composition of $\gamma$ (at%)	900°C
F.GP	$\gamma'$ amount (at%)	900°C
DENSITY	Density (g/cm ³ )	RT
SI	Solution Index	900°C
LAT.GP	Lattice parameter of $\gamma'$ (Å)	RT
LAT.G	Lattice parameter of $\gamma$ (Å)	RT
LM	Lattice misfit (%) = $(a\gamma' - a\gamma)/a\gamma$	RT
NV.GP	Electron vacancy number of $\gamma'$	900°C
NV.G	Electron vacancy number of $\gamma$	900°C
NV.G-NVC	Barrows' PHACOMP	900°C
LIQ	Liquidus temperature (°C)	—
SOL1	Solidus temperature (°C)	—
RANGE	Melting range (°C)	—
SOL2	Incipient melting temperature (°C)	—
SOLV	Solvus temperature (°C)	—
WDW	Solution temperature range (°C)	—
H.COR.C	Metal loss by hot corrosion (Ratio to IN738) —Crucible test—	900°C
H.COR.B	Penetration by hot corrosion (Ratio to IN738) —Burner rig test—	850°C
YS	Yield stress (Mpa)	900°C
UTS	Ultimate tensile strength (Mpa)	900°C
EL	Tensile elongation (%)	900°C
LIFE.CC	Creep rupture life as CC structure (h)	1000°C·12 kgf/mm ²
LIFE.SC	Creep rupture life as SC structure (h)	1040°C·14 kgf/mm ²
SPC.STRGTH	Specific strength as CC structure (MPa/(g/cm ³ ))	980°C·100h

RT: Room Temp.

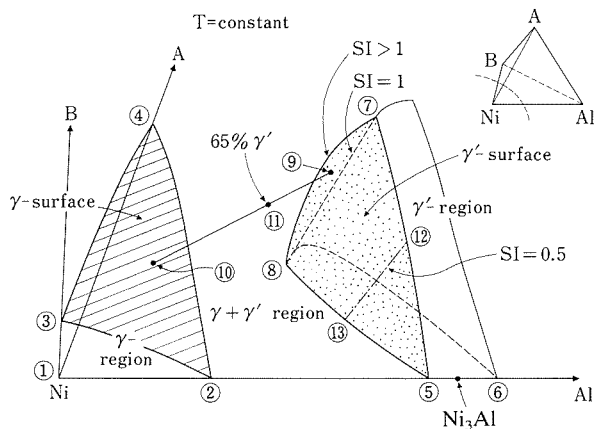


Fig. 9 Ni corner of Ni-Al-A-B quaternary system to show  $\gamma$  and  $\gamma'$  equilibrium and alloy design.

general trend, according to the above mentioned principle, higher creep rupture strength alloys showed lower hot corrosion resistance. At a given hot corrosion resistance level, developed alloys gave creep rupture strengths higher than those of commercial alloys, mainly due to the adoption of higher SI values in  $\gamma'$ , see Fig. 10. Of these developed alloys, alloy TM-321¹¹⁾ was proposed for the first stage blade of the Advanced Gas Turbine of the project. This alloy has a higher rupture strength than that of alloy Mar-M247, the both being similarly poor in hot corrosion resistances. The adoption of alloys with poor hot corrosion resistances were considered possible because the turbines in the project were designed to be run by natural gas which is low in sulfur content. The composition and temperature capability of alloy TM-321 are shown in Table 1 and Fig. 11, in which alloy Mar-M247 is also shown.

Metal temperatures of nozzles are generally higher than those of blades. For the nozzles, Alloy TM-269 was proposed, which had been designed to have a melting temperature higher than those of alloys Mar-M247 and TM-321 as well as a high strength comparable to that of alloy Mar-M247. In alloy TM-269, those intentions were not realized completely but this was used as a model alloy for the second nozzles in the gas turbine of the project. The composition of this alloy is shown in Table 1.

Melting stock manufacture process was studied by Daido Steel Ltd.²⁾ Investment casting of air-cooled

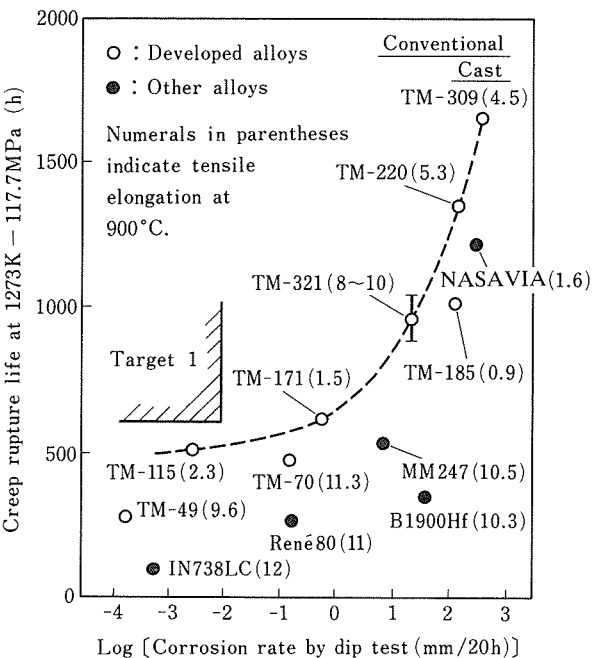


Fig. 10 Creep rupture life (in air) of CC alloys vs. hot corrosion rate. Corrosion test: 75%Na₂SO₄+25% NaCl molten salt at 1173 K.

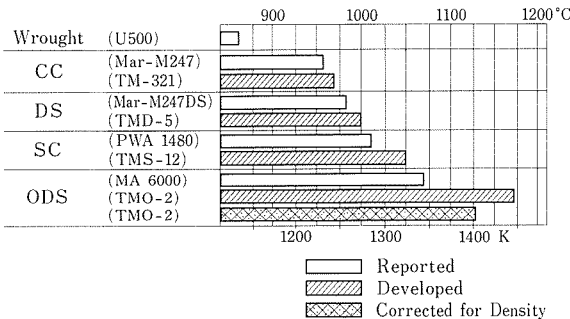


Fig. 11 Temperature capability to give a 1000 h rupture life at 137.3 MPa for Ni-base superalloys shown in Table. 1. CC: Conventionally cast alloy, DS: Directionally solidified alloy, SC: Single crystal alloy, and ODS: Oxide dispersion strengthened alloy. Hatched bars indicate developed alloys.

blades was studied by Mitsubishi Metals Co. Ltd.,²⁾ and Komatsu-Hawmet corporation was also incorporated. The air-cooled second stage nozzles were cast by Hitachi Metals Co. Ltd.²⁾

Photo 1(a) shows an air-cooled hollow blade made by Alloy TM-321.

Aluminide coating and thermal barrier coating were studied by NRIM and Toshiba Co. Ltd.; the Y-doped (PVD) aluminide coating (NRIM)¹²⁾ and the

automated plasma spray coating technique (Toshiba)^{2),13)} were developed.

## 6. DIRECTIONALLY SOLIDIFIED (DS) COLUMNAR Ni-BASE ALLOYS

Grain boundary cracking in service is reduced in DS alloys with columnar crystals due to the reduction of stress perpendicular to grain boundaries. Cracking between columnar crystals in the solidification process can occur in some alloys with inappropriate compositions. This is caused, just after solidification, by expansion stress from a core to make an air-cooled hollow blade. To avoid this problem in DS alloys we found that  $\gamma'$  phase contents in alloys had to be controlled below a certain level.

Our target was to develop an alloy superior to alloy Mar-M247DS without the above mentioned cracking. We picked up one of our strongest CC alloys and changed  $\gamma'$  contents without changing, on the alloy design basis,  $\gamma$  and  $\gamma'$  phase compositions within a range of 50 to 62%. From the standpoint of creep rupture strength, higher  $\gamma'$  phase contents are preferable, so we chose the highest content of the phase that did not cause grain boundary cracking during solidification process as is shown in Fig. 12. Thus alloy TMD-5 with 55% of  $\gamma'$  phase was developed.¹¹⁾ The composition is given in Table 1. The properties of this alloy is superior to those of Mar-M247DS, as shown in Table 3 and Fig. 11.

Daido Steel Co. Ltd. again prepared melting stocks of this alloy. Ishikawajima-Harima Heavy Industries Ltd. (IHI) studied manufacturing of hollow DS blades¹⁴⁾ and also contributed in determining the composition of alloy TMD-5.¹⁴⁾

Photo 1(b) is an air-cooled DS hollow blade cast by IHI using alloy TMD-5.

## 7. SINGLE CRYSTAL Ni-BASE ALLOY (SC)^{3),4)}

The target for SC alloys was as follows:

Rupture life at 1313 K and 137.3 MPa is more than 1000 h, and rupture elongation at the same condition is more than 10%.

MRIM used their alloy design program described above for SC alloys. Important factors taken into

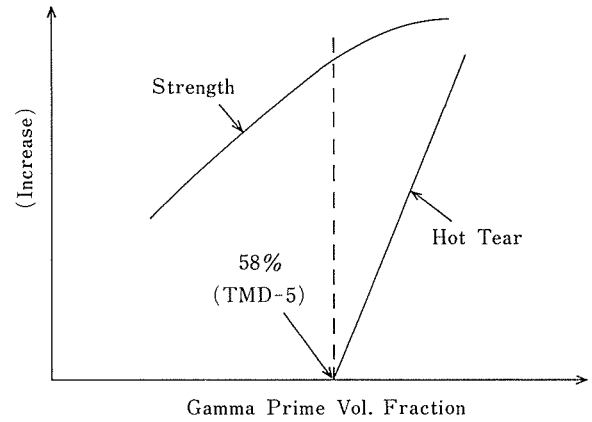


Fig. 12 Schematic diagram to show the selection of  $\gamma'$  volume fraction for DS alloy not to induce hot tear by cores.

Table 3. Properties of DS alloys (longitudinal), MM 247 (commercial alloy, its composition is shown in Table 1 as MM247 (DS)) and TMD-5 (developed alloy, its composition is also shown in Table 1). Testing condition for low cycle fatigue: 1173 K and strain rate 0.1%/s (tension/compression).

Alloy	Creep rupture test (1273 K, 117.7 MPa)		Cycles to failure in low cycle fatigue	
	Life (h)	El. (%)	Total strain range 1.5 (%)	1.0 (%)
MM247	840	14	367	1060
TMD-5	3540	14.8	615	4068

Testing condition for low cycle fatigue: 1173 K and strain rate 0.1%/sec(tension/compression)

consideration for SC alloy development were gamma-prime volume fraction, lattice mismatch of gamma and gamma-prime phases, W/t_a ratio in gamma-prime, solid solutioning degree of gamma-prime (according to our terminology, SI, as described above), and solution treatment temperature allowance (window).

Alloy TMS-12, shown in Table 1 and Fig. 11, is our first alloy proposed for the project.¹⁵⁾ Later, many other SC alloys were proposed,^{16),17),18)} as is shown in Table 4 and Fig. 13. Some of them are well within the target area shown in Fig. 13.

Near the end of the project, the second version of alloy design program was developed as described



**Table 4.** Compositions of some developed Ni-base single crystal (SC) alloys (Mass %).

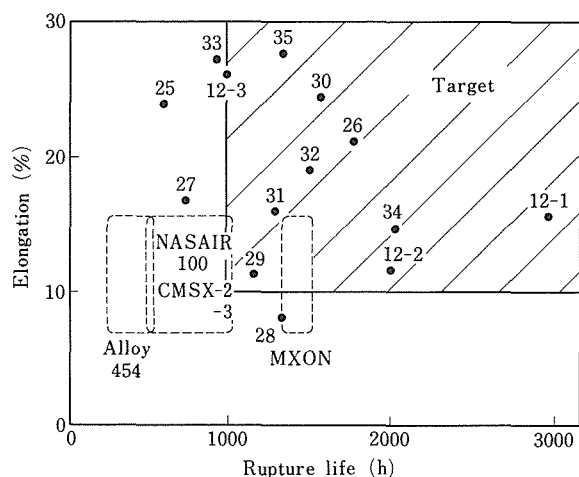
Alloy	Ni	Co	Cr	Mo	W	Al	Ti	Nb	Ta	Re	$\gamma'$	SI	Ta/W	$\delta$
TMS-31	bal.	7.64	5.88	—	17.10	4.70	—	—	4.87	—	58	1.39	0.51	0.35
TMS-32	"	7.74	5.94	—	16.11	5.08	—	—	4.52	—	59	1.30	0.49	0.34
TMS-33	"	7.90	6.04	—	14.88	5.44	—	—	4.15	—	59	1.20	0.49	0.35
TMS-34	"	7.92	6.02	—	15.19	5.02	—	—	5.45	—	60	1.32	0.61	0.40
TMS-35	"	8.03	6.02	—	13.71	4.97	—	—	6.61	—	61	1.32	0.82	0.51
TMS12-1	"	—	6.65	—	13.56	4.62	—	—	8.09	—	61	1.40	1.01	0.55
TMS12-2	"	—	6.66	—	12.75	4.96	—	—	7.49	—	61	1.30	1.00	0.54
TMS12-3	"	—	6.67	—	11.74	5.31	—	—	7.08	—	61	1.20	1.03	0.55
TMS-25	"	7.91	5.56	—	13.11	5.13	—	—	7.49	—	64	1.33	0.92	0.57
TMS-26	"	8.22	5.61	1.85	11.07	5.02	—	—	7.70	—	64	1.33	1.12	0.36
TMS-27	"	8.22	5.95	—	12.81	4.84	0.91	—	2.10	—	64	1.32	0.76	0.53
TMS-28	"	8.56	5.88	1.86	11.25	4.77	0.90	—	6.06	—	65	1.34	0.86	0.30
TMS-29	"	8.69	6.02	1.87	11.33	4.78	0.93	0.86	4.40	—	66	1.35	0.61	0.25
TMS-30	"	7.73	5.37	—	10.54	5.28	—	—	8.11	2.5*				

 $\delta=100\times\delta$ ;  $\delta$ : defined as below

* addition

 $\delta$ : 2 (lattice parameter of gamma prime—lattice parameter of gamma)/(lattice parameter of gamma prime + lattice parameter of gamma).

SI: Solution Index (An index to define the degree of solid solution of gamma prime phase).

**Fig. 13** Creep rupture properties of some developed Ni-base single crystal (SC) superalloys at 137.3 MPa and 1313 K. Numerals above data points indicate alloy numbers in Table 4. Areas of dotted lines show the properties of some commercial or reported alloys at the beginning of the project (Advanced Alloys).

above,⁶⁾ in which many pairs of gamma and gamma-prime compositions gained through intricate analyses by EPMA were utilized. In this program some sets of regression equations for alloy properties were also renewed. In this version the lattice mismatch played an important role and by running this program some

high Mo alloys were indicated to have higher creep rupture strengths with lower density values. The most probable high Mo light alloy is TMS-62,¹⁹⁾ and its composition is shown in Table 1.

Melting stocks with low impurities and accurate concentrations of component elements were provided by Daido Steel Co. Ltd.²⁰⁾

Making good cores is one of the important techniques for single crystal hollow blades. This was investigated by Government Industrial Research Institute, Nagoya.²¹⁾ Cores must be held in molten alloy for about half an hour without damage and, after solidification, must be removed by leaching in an alkaline solution; this second condition requires that the base substance is silica which does not belong to the highest heat resistant ceramics. The main remedies adopted were using fused silica of appropriate powder sizes, crystallization rate of fused silica being controlled less than 10% during sintering, dispersion of crystalline ceramics, and using injection molding. A good composition and process was proposed, and according to the proposal IHI made excellent cores for making experimental SC blades. The injection molding of ceramics parts is a new technology and is expected to be applied to other fields.

IHI, Ltd., Hitachi, Ltd. and Hitachi Metals, Ltd. performed experiments for producing SC blades and evaluating them.^{22),23)} Plasma beam skull remelting was applied to an experimental SC making furnace to minimize the contamination during remelting of melting stock.²²⁾ To another experimental furnace was applied a static magnetic field to reduce convection, but the result was not as expected.²³⁾

Solidification simulation models were used to analyze temperature distribution during solidification.^{22),23)} Flat solidification front is required to make a single crystal article; otherwise at the outer surface of the article other crystals would nucleate. The solidification models could show conditions to get a flatter solidification front.

Developed alloys and cores were tested to make hollow blades. Some improvements were further required in them; solution heat treatment caused recrystallization at the strained portion of a blade such as the platform and deformation for the cores was sometimes observed.²⁴⁾ Photo. 1(c) shows an SC hollow blade made by IHI using Alloy TMS-32, one of SC alloys proposed by NRIM.

## 8. SUPERPLASTICALLY WORKABLE Ni-BASE ALLOYS^{3),4)}

The target for this type alloy in the project was as follows.

The UTS at 1033 K is more than 1569 MPa, tensile elongation at that temperature is more than 20%, and the alloy must be superplastically forged at around 1300 K using a preform made by HIP.

After the project started it was found that this target, except superplasticity, was too high to be achieved.

The alloy is to be used for gas turbine disk materials. As is described before, preforms for superplastic forging were intended to be made without an extrusion process to avoid the usage of a big extrusion machine, which is not economical and practically can not be installed. Consequently, preforms were made through HIP-processing of powders without extrusion.

For the alloy design, the above described alloy

design program by NRIM for Ni-base alloys was applied to calculate  $\gamma$  and  $\gamma'$  compositions to be present in P/M Ni-base superalloy, RENE 95, and a series of alloys, including the original alloy, RENE 95, with various gamma-prime contents using the compositions of the two phases calculated to be present in RENE 95 were designed. An alloy, TMP-3 designed to have a  $\gamma'$  content a little higher than the one in the original alloy showed better superplasticity than that of the original.²⁵⁾ NRIM proposed this as an official candidate alloy for the process research works, though the alloy did not satisfy the target.

NRIM continued research works to get alloys with higher strength and elongation values through composition modifications as well as heat treatments and some doping.²⁶⁾ Stronger alloys were developed. An improved regression equation for strength was then developed, and this showed that we would be able to design alloys with still higher strengths, which, however, did not reach the target value.²⁷⁾

Melting stocks to be remelted for powder production were made by Daido Steel Co., Ltd. Two processes for powder making were employed. The first one was the argon gas atomization (by Kobe Steel, Ltd.) and the second the liquid helium cooling centrifugal atomization (Daido Steel Co.).²⁷⁾ The first one is rather conventional and by this good powders were produced but the second was proved to be further studied for improvement.²⁷⁾ Most isothermal superplastic forging experiments were done with powders made by the first method. For the second process a high speed rotating disc brought about some difficulty.

Kobe Steel designed and constructed a superplastic forging equipment and made discs 400 mm in diameter from HIP preforms of gas atomized powders of alloy TMP-3.²⁸⁾ A computer calculation model utilizing the finite element method was applied to determine the shape of the preform to give uniform deformation. Kobe Steel also developed dual property discs made of two alloys.²⁸⁾

Sumitomo Electric Industries, Ltd. treated powders in an attritor to give them strain.²⁹⁾ The strain induced in powders was expected to promote recrystallization of them and hence grain size reduction. The attritor

treated powders, after HIP consolidation, showed improved superplasticity. Impurities introduced by this treatment sometimes reduced the mechanical properties after superplastic deformation but this was avoided by careful attritor treatment. It was also shown that attritor-treated powders could be consolidated by CIP followed by sintering to make preforms for superplastic forging.

Hitachi, Ltd. made superalloy ribbons by the melt spinning method.³⁰⁾ Those ribbons showed superplasticity and were tested as inserts for diffusion bonding of cast superalloys.

## 9. OXIDE DISPERSION STRENGTHENED(ODS) Ni-BASE ALLOYS^{3),4)}

### 9.1 Outline

ODS alloys, made up of  $\gamma$ ,  $\gamma'$  phases and yttria particles, are stronger than SC alloys and expected to be used as materials for gas turbines. Mechanical alloying in an attritor, extrusion, forging, zone annealing, and bonding are usually considered to be applied to make ODS blades.

NRIM again proposed a candidate alloy; this alloy was named TMO-2.^{31),32)} A previously developed conventionally cast alloy, TM-220, which is one of the strongest alloys as CC alloys, was modified by the alloy design method to get alloy TMO-2. The composition of TMO-2 is shown in Table 1. This alloy, compared to alloy MA 6000 is higher in W and gamma prime contents.

The target for ODS alloy in the project (Advanced Alloys) was as follows.

Rupture life at 1373 K and 137.3 MPa is more than 1000h, and rupture elongation at that condition is more than 5%.

Alloy TMO-2 gave a rupture life much longer than the target value and hence than that of alloy MA 6000 (Fig. 11), but the elongation value was about 4% or less, being probably similar to that of alloy MA 6000.

NRIM improved intermediate temperature strength of this type alloy by further increasing  $\gamma'$  content of alloy TMO-2, to get, for instance, alloy TMO-20 which was designed to have a  $\gamma'$  content of

75%.^{31),32)}

This section 9 for ODS alloys is arranged to be a little more detailed than other sections due to the potential importance of this type of alloys.

### 9.2 Introductory Remarks

Oxide dispersion strengthened (ODS) Ni-base superalloys are considered to have potential applications in many high temperature services. Especially, ODS alloys having high  $\gamma'$  contents are candidate materials which can be used for gas turbine blades instead of Ni-base single crystal alloys. The mechanical alloying technique developed by J. Benjamin³³⁾ was applied to high  $\gamma'$  type Ni-base alloys to develop alloy MA6000.³⁴⁾ This alloy, though it has not been used extensively for gas turbine or jet engine blades, many studies have been done for its processes, properties and applications.

The above mentioned alloy design technique was applied to develop Ni-base ODS superalloys of high volume fractions of  $\gamma'$  phase. The alloys are for gas turbine or jet engine blades. As in the other alloy developments in the project (Advanced Alloys), the authors' group in NRIM was in charge of proposing new alloy compositions. Three companies as members of this project did ODS process studies by using the proposed composition. The three companies also helped the author and his group make their ODS specimens.

### 9.3 Development of Alloy TMO-2

We started from one of the strongest Ni-base conventionally cast superalloys developed previously by the authors' group by using the above mentioned alloy design method. It was alloy TM-220 (see Table 5). This alloy was designed to have 65 vol. % of  $\gamma'$  phase. We considered that this  $\gamma'$  volume fraction was a little too high to begin with, and we set the fraction at 55%. We also considered that W content of alloy TM-220 is high and Cr content a little too low, from density and hot corrosion points of view, respectively. From those considerations, we designed alloys TM-303 and TMO-2, the former being a conventionally cast alloy and the latter an ODS one (see Table 5). Alloy TM-303 was tested as a reference alloy in cast form; this has no yttria and contains a higher C content than alloy TMO-2.

**Table 5.** Compositions of ODS alloys and reference alloys (mass %) and compositions of phases in the alloys calculated by the alloy design program (atomic %).

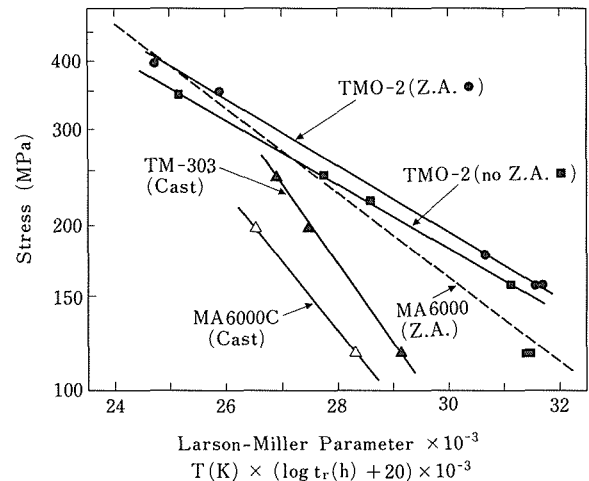
Alloy	$\gamma'$ (%)	Ni	Al	Co	Cr	Ti	Ta	W	Mo	Y ₂ O ₃	Note
TM-220	65	58.9	4.9	9.0	5.2	1.0	3.7	14.6	1.8		Hf:0.8, C: 0.11
TM-303	55	59.1	4.2	9.9	6.0	0.8	4.8	12.5	2.3		Hf: 0.6, C: 0.1
TMO-2	55	58.4	4.2	9.7	5.9	0.8	4.7	12.4	2.0	1.1	
$\gamma'$ phase	(at%)	65.0	16.4	7.8	2.7	1.8	2.4	3.4	0.5		
$\gamma$ phase	(at%)	62.9	2.7	13.9	12.6	0.2	0.6	5.0	2.2		
TMO-19	0	55.8	1.1	12.4	9.9	0.2	1.9	14.3	3.2	1.1	
TMO-9	35	57.7	3.1	10.7	7.4	0.6	3.7	13.1	2.4	1.1	
TMO-8	45	58.3	3.7	10.2	6.6	0.7	4.3	12.7	2.2	1.1	
TMO-7	65	59.5	4.9	9.2	5.1	1.0	5.4	12.0	1.7	1.1	
TMO-20	75	60.1	5.5	8.7	4.3	1.1	6.0	11.6	1.5	1.1	
TMO-21	55	59.5	4.4	9.8	5.9	0.9	4.9	12.5	2.0	—	
MA 6000	52	68.4	4.6	—	15.2	2.5	2.0	4.0	2.0	1.1	Zr: 0.15
$\gamma'$ phase	(at%)	72.8	15.5		3.9	5.2	0.8	0.8	0.8	0.5	
$\gamma$ phase	(at%)	62.7	3.5		29.6	0.5	0.2	1.4	1.9		

C: 0.05, B: 0.01, Zr: 0.05.

Compositions of  $\gamma'$  and  $\gamma$  phases and volume fraction of  $\gamma'$  phase of alloy MA6000 was calculated by our program and are also given in Table 5.

Creep rupture tests were conducted for those alloys and the results are shown in Fig. 14. Alloy TMO-2 shows superb creep rupture strengths at higher temperatures and it satisfies the official target of the project. The creep rupture elongation values were, however, 2 to 4% and they were lower than the target value (5%).

The microstructure of alloy TMO-2 (isothermally annealed resulting in elongated grains) creep-tested and interrupted at about 50,000 hours was observed. This specimen, after tested for 50,000 hours at 1273 K (1000°C) and a stress of 117.7 MPa (12 kgf/mm²), showed virtually no deformation. This is considered to be the evidence for the existing of the threshold stress in ODS alloys.³⁵⁾ The observation of this specimen also shows that structure of alloy TMO-2 is quite stable even after heating for 50,000 hours at 1273 K (1000°C), except some thin  $\gamma'$ -renuded zones at the surface. The diameter of this specimen showed no reduction after the test; this also shows that the alloy is sufficiently oxidation-resistant at this temperature.



**Fig. 14** Creep rupture lives of ODS alloy TMO-2 and other alloys to be compared, expressed by Larson Miller Parameters vs. stress. Alloys TM-303 and MA6000C are conventionally cast alloys having the compositions same as those of alloys TMO-2 and MA6000, respectively, except that the former alloys are free from yttria and contain higher C contents. Z.A. and no. Z.A. stand for zone-annealed and isothermally-annealed, respectively.

#### 9.4 Effect of $\gamma'$ Volume Fraction on creep³⁶⁾

It is known that ODS alloys are not so strong at intermediate temperatures such as 1000 K. To improve intermediate temperature strengths, the increases in  $\gamma'$  volume fractions were intended. For this

purpose we studied the effect of  $\gamma'$  volume fractions on creep properties.

The  $\gamma$  and  $\gamma'$  phase compositions designed to exist in alloy TMO-2 were used to make alloys with various amounts of  $\gamma'$  phase, and thus we obtained a series of alloys with different amounts of  $\gamma'$  phase with the fixed (on the design basis, of course) compositions of  $\gamma$  and  $\gamma'$  phases.

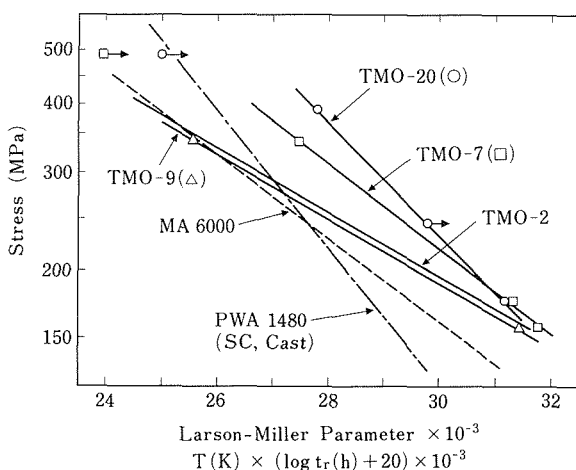
**Fig. 15** shows the creep rupture test results for those alloys; see Table 5 for their compositions. It is seen that the intermediate temperature strengths of alloys TMO-7 and TMO-20 are improved; they are higher than those of a single crystal Ni-base superalloy PWA 1480.

The same data are plotted in **Fig. 16**. This shows that the increase of  $\gamma'$  phase improves intermediate temperature strengths as is shown in literature.³⁷⁾ **Fig. 17** shows that the increase of  $\gamma'$  phase is also effective for lowering intermediate temperature steady state creep rates.

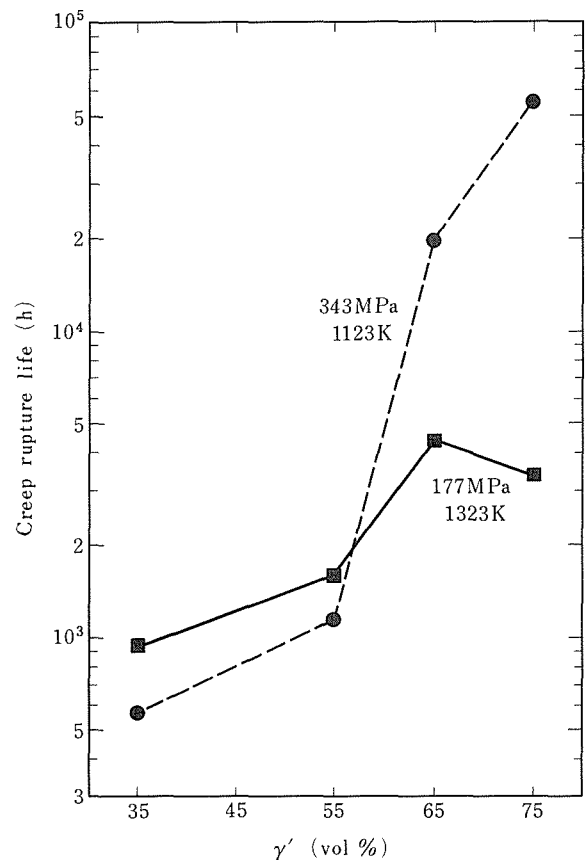
**Fig. 18** shows the result of texture measurements by X ray. A  $\{111\}$  texture develops by increasing  $\gamma'$  phase volume fraction. It is known that this orientation is favorable for creep next to  $\{100\}$  orientation in single crystal experiments.

### 9.5 Effect of $\gamma'$ Volume Fraction on Secondary Recrystallization Response³⁸⁾

Secondary recrystallization responses of extruded



**Fig. 15** Creep rupture lives (expressed by Larson Miller Parameters vs. stress) of developed ODS alloys with various amounts of  $\gamma'$  phase (see Table 5). For reference, alloy MA6000 (ODS) and alloy PWA1480 (single crystal alloy) are shown. ODS alloys are all zone-annealed.



**Fig. 16** Effect of  $\gamma'$  phase volume fractions of developed ODS alloys on creep rupture lives.

bars (primarily recrystallized) are important for ODS materials. Elongated grains of aspect ratios greater than about 7 are required for good creep rupture properties.³⁹⁾ When alloys show good secondary recrystallization by isothermal annealing, they can give good elongated grains by zone annealing. Consequently we examined secondary recrystallization responses of alloys by isothermal annealing.

**Fig. 19** shows Vickers hardness changes of extruded bars of alloys with various amounts of  $\gamma'$  phases. From this figure and SEM observations of specimens, secondary recrystallization temperatures were obtained and are plotted in **Fig. 20** as a function of  $\gamma'$  phase volume fractions.

**Fig. 21** shows primarily recrystallized grain size of as extruded bars as a function of  $\gamma'$  phase volume fractions.

By comparing the results of the above two figures, we can say that secondary recrystallization tempera-

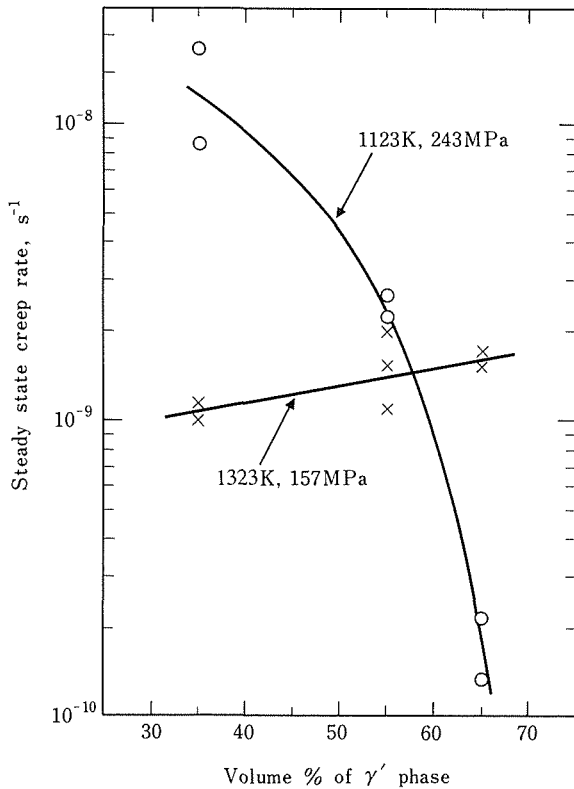


Fig. 17 Effect of  $\gamma'$  phase volume fractions of developed ODS alloys on steady state creep rate.

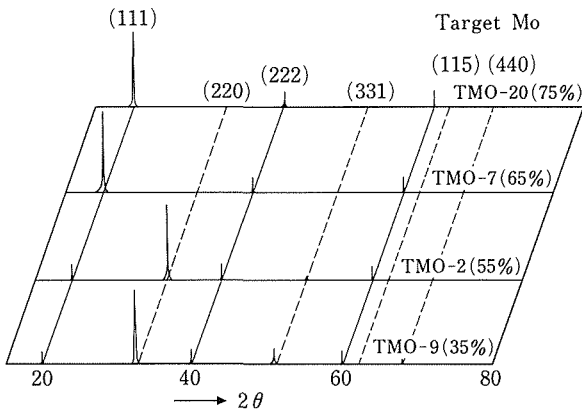
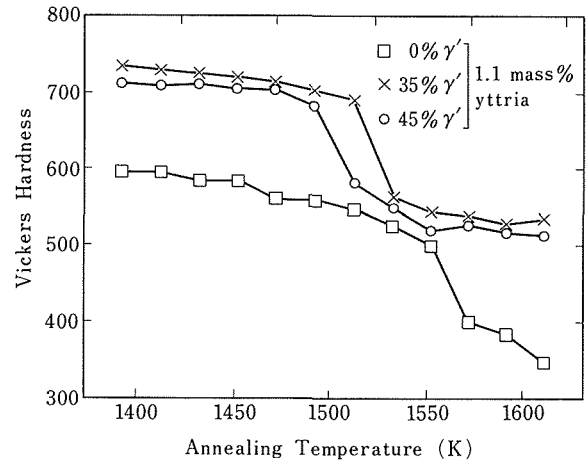
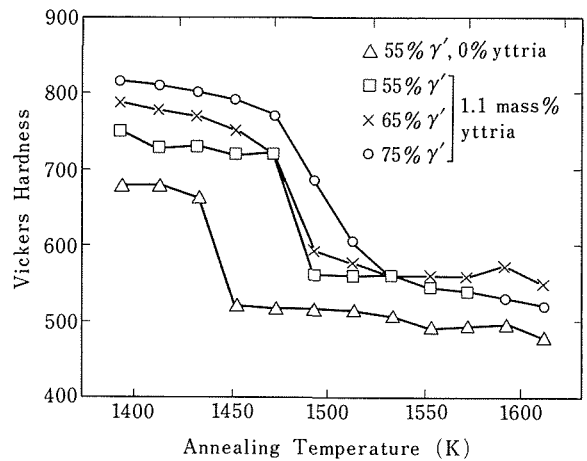


Fig. 18 Effect of  $\gamma'$  phase volume fractions of developed ODS alloys on X-ray diffraction patterns (after zone annealing) indicating the development of a favorable {111} texture by increasing  $\gamma'$  phase volume fraction up to 75%.

tures decrease as primary recrystallization grain sizes decrease by increasing  $\gamma'$  phase amounts. At around 60% of  $\gamma'$  phase, the secondary recrystallization temperature coincides with the  $\gamma'$  phase solvus temperature. Beyond this  $\gamma'$  phase volume fraction,



(a)



(b)

Fig. 19 Vickers hardness of ODS alloys isothermally annealed at various temperatures for 1 h.

(a): Alloys of  $\gamma'$  phase volume fractions of 0 to 45%.  
(b): Alloys of  $\gamma'$  phase volume fractions of 55 to 75%.

the secondary recrystallization is triggered by  $\gamma'$  dissolution and hence the recrystallization temperature goes up with increasing  $\gamma'$  phase amounts.

Fig. 22 shows the effect of yttria contents on secondary recrystallization temperature (SRx) for the case of 55 volume % of  $\gamma'$ . The addition of yttria reduces the primary recrystallization grain size (Fig. 21). In spite of this effect, the addition of yttria retards the secondary recrystallization.

## 9.6 Process Studies by Companies for ODS Alloys

Alloy TMO-2, and sometimes alloy MA 6000 as a reference material, were used for studying processes

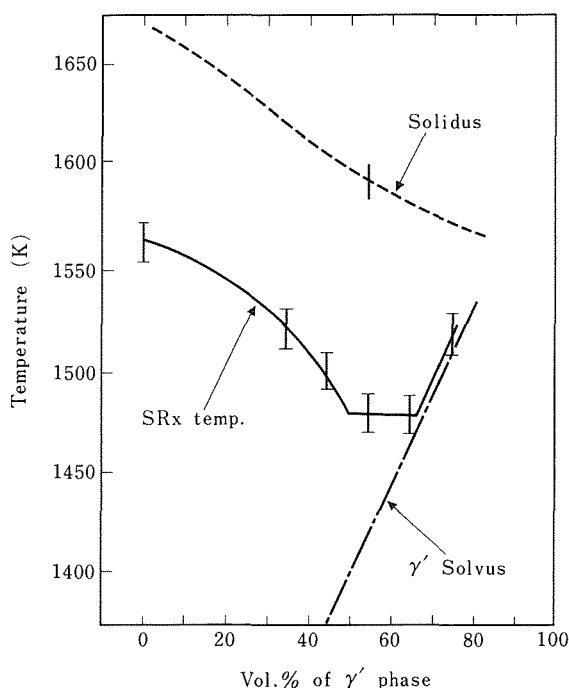


Fig. 20 Effects of  $\gamma'$  phase volume fractions on secondary recrystallization (SRc) temperatures of ODS alloys containing 1.1 mass % of yttria.

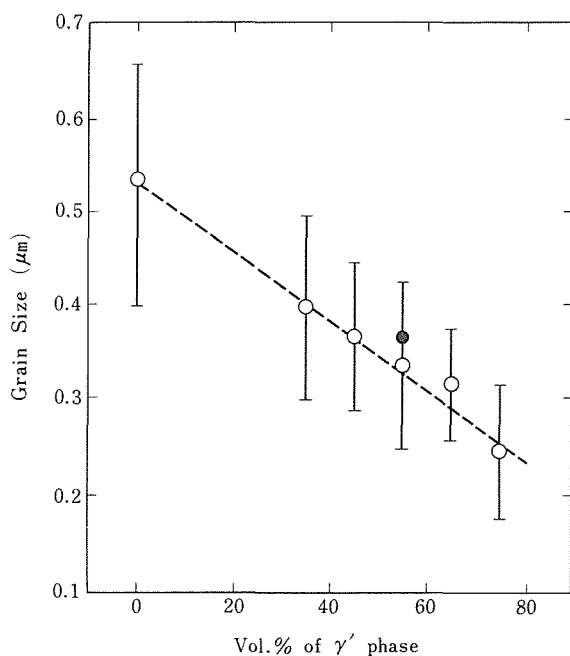


Fig. 21 Effect of  $\gamma'$  phase volume fractions on primary grain size (grain size of as extruded materials) of ODS alloys. A closed data point is for alloy without yttria (processed like as ODS alloy) and others for alloys with 1.1 mass % yttria.

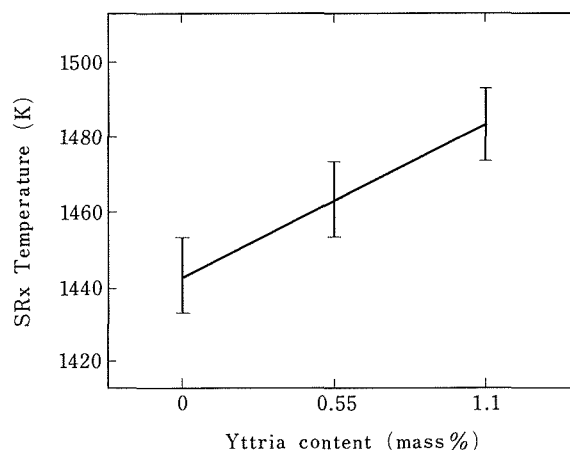


Fig. 22 Effect of yttria contents on secondary recrystallization (SRc) temperature for alloys with 55% of  $\gamma'$  phase.

of ODS alloy.

Sumitomo Electric Industries, Ltd. took part in mechanical alloying and extrusion.⁴⁰⁾ After trying to find appropriate conditions, they succeeded in making good extruded bars of alloy TMO-2. The bars were 30–40 mm in diameter, high in hardness (as high as Hv 800), ready to be recrystallized, and isothermally forgeable.

Kobe Steel, Ltd. forged isothermally bars of alloy TMO-2 to give crude blade shapes.⁴¹⁾ To make a hollow blade, the whole blade was divided into two parts or two sides. The two sides are to be bonded in later stage of the process; this type of blade was named a twin blade. It is known that high gamma-prime ODS alloy must be recrystallized for strengthening, and this forging process gives a bad effect to this recrystallization property of the alloy. Kobe Steel Ltd. succeeded in forging blades, sound and recrystallizable, without platform portions, but some improvement was required to forge a blade with platform which can be recrystallized.

IHI was in charge of the final stage of the process.⁴²⁾ Zone annealing of forged bars is rather a difficult problem, because its shape is not uniform. One side of a twin blade before bonding was put into a divided mold to make the assembled article as if it were a solid round bar. This was then zone annealed. This process was found effective if there was little clearance between the molds and the forged article inside. IHI did an experiment to give information for

forging condition that is good for zone annealing recrystallization. Bonding of ODS alloys is known to be a difficult process. Solid state bonding without insert materials and TLP bonding were tried. The bonding strengths were not sufficient.

###### 10. SUPERPLASTIC Ti ALLOYS^{3),4)}

Ti alloys were developed to be applied to gas turbine compressor discs. Superplastic forging was used for this purpose with preforms made from HIP. Extrusion process was not applied to make preforms to avoid installation of a big extrusion machine.

The target of the project for Ti alloys was as follows.

Specific strength at 573 K is more than  $27.46 \times 10 \text{ Nm/kg}$ , or  $28 \text{ (kgf/mm}^2\text{)/(gr/cm}^3\text{)}$ , elongation at the same condition is more than 10%, and the alloy must be superplastically forged to disc shapes with preforms made by HIP.

NRIM was in charge of proposing new alloys satisfying the target. Three types of alloy design methods, Methods A, B, and C were tried. In principle, in all the methods,  $\alpha$  and  $\beta$  phase compositions at superplastic forging temperatures (1020 to 1170 K) are calculated, and alloys with a phase volume fraction ratio of 1:1 at superplastic forging temperatures were designed. Some properties, such as  $m$  values for superplasticity, were estimated by equations developed.

Three methods, A, B, and C were used to calculate  $\alpha$  and  $\beta$  phase compositions in multicomponent Ti systems. Method A depends on the syntheses of related Ti-X phase diagrams⁴³⁾ and Method B utilizes compositions of the two phases by EPMA Method C⁴⁴⁾, a thermodynamical one, depends on Hillert's subregular solution model. Recently, we are trying sublattice model calculations to incorporate the effect of oxygen and also to treat  $\alpha_2$  phase.⁴⁵⁾

Table 6 shows compositions of some Ti alloys developed. Fig. 23 shows the tensile properties of these alloys together with those of some representative commercial alloys. Alloys GT-33, GT-60, and Gt-61 satisfied the target of the project. All the alloys

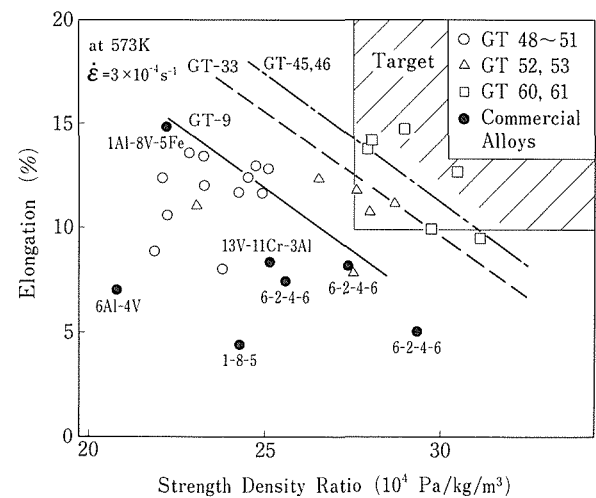


Fig. 23 Tensile properties of developed Ti alloys (Table 6) and some commercial Ti alloys (6-2-4-6: 6Al-2Sn-4Zr-6Mo, 1-8-5: 1Al-8V-5Fe) at 573 K (300°C). Elongation in this figure is not superplastic one.

Table 6. Chemical compositions of developed Ti alloys (mass %).

Alloy	Al	Sn	Zr	V	Mo	Cr	Fe	O	Ti
GT-9	5.7	1.4	3.9	0.5	1.0	1.3	1.0	0.12	Balance
GT-33	6.5	1.4	1.0	1.4	2.9	2.1	1.7	0.11	"
GT-45	6.4	0.9	1.1	2.9	2.5	2.5	1.6	0.11	"
GT-46	5.7	0.9	5.1	1.5	2.5	3.5	2.6	0.16	"
GT-48	6.31	1.68	1.84	0.54	0.53	0.52	3.04	0.10	"
GT-49	6.24	1.56	1.82	0.74	1.13	0.49	2.33	0.10	"
GT-50	5.88	1.52	3.85	0.73	0.51	0.49	2.31	0.10	"
GT-51	6.06	1.52	3.90	0.53	1.13	0.49	1.95	0.10	"
GT-52	6.56	1.06	1.01	0.90	3.57	0.49	2.81	0.11	"
GT-53	6.91	1.03	1.02	0.90	1.51	3.20	1.33	0.11	"
GT-60	7.16	0.47	1.03	1.79	0.51	0.86	3.17	0.10	"
GT-61	6.71	1.31	1.97	1.97	0.49	0.59	2.69	0.11	"



developed shown in Table 6 have fairly good superplastic properties. Note that elongation values in Fig. 23 are not superplastic ones.

Mitsubishi Metals Ltd. studied processes for manufacturing powders and forging discs using the developed alloy GT-33 (Table 6).⁴⁶⁾ Powders were made by a plasma beam rotary electrode process. Discs of around 400 mm in diameter were successfully forged superplastically from preforms of alloy GT-33 powders consolidated by HIP.

## 11. CONCLUDING REMARKS

Quite a many developmental studies had been done for conventionally cast Ni-base alloys. Since there were found no effective ways to improve grain boundaries at high temperatures except so far known techniques, we could not get great improvements in creep rupture strengths in this type of alloys. Improvements in matrices of gamma and gamma-prime phases were possible, but cracking in grain boundaries limited the overall creep rupture strengths.

We did not do so many experiments for selecting compositions of DS alloys, however, similar limitations were expected for cracking in columnar crystal boundary.

For SC alloys, we believe there still be much work to be done for their compositional modifications. Due to some technical difficulties in ODS alloys, SC alloys will probably continue, at least for 10 years or so, to be used in engines and turbines. For SC alloys, however, an increase in temperature capability of 30 to 50 K would be the limit.

Irrespective of our expectation at the start of the project, increases in tensile strengths at 1033 K of P/M Ni-base superalloys for turbine discs were quite difficult. Tensile strengths at temperatures as low as 970 K can be improved anyhow, a temperature increase such as 50 K from this, however, causes a rather sharp decrease in tensile strengths. Superplastic elongation, per se, can be rather easily attained. However, the detrimental effects of superplastic deformation on some properties should be more carefully studied.

ODS Ni-base superalloys for gas turbine blade materials still remain future candidate materials.

Manufacturing of complicated blades and interaction between this and properties of alloys after the manufacturing processes should be studied more comprehensively by taking the effects of alloy compositions into consideration.

We obtained many Ti alloys having superior tensile properties at 573 K. Air temperatures in recent turbine or jet engine compressors go up to about 900 K, and at such temperatures creep resistances rather than tensile strengths should be considered for the selection of alloys. Creep resistances of Ti alloys having high tensile strengths are not necessarily high. We are now intending to improve creep properties of Ti alloys by incorporating some limited amounts of  $\alpha_2$  phase, which is usually considered as a detrimental phase for ductility.

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