# Design and Development of Superalloys in Japan

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### Abstract

We had two national projects in which superalloys were developed. The first one was "Advanced Gas Turbine"; in this project we treated conventionally cast nickel-base superalloys and directionally solidified nickel-base superalloys. Those alloy developments started in 1978 and ended in 1984. The second one, 1981 to 1988(fiscal), was "Advanced Alloys with Controlled Crystalline Structures"; single crystal nickel-base superalloys, superplastically workable nickel-base P/M alloys, and oxide dispersion strengthened nickel-base superalloys were treated. This paper briefly reviews the alloy developmental studies and process studies carried out in the two projects.

### Introduction:

Agency of Industrial Science and Technology(AIST) of MITI planned and sponsored two national projects in which various types of nickel-base superalloys were developed. "Advanced Gas Turbine" was the first one and this project dealt with conventionally cast nickelbase superalloys (CC alloys) and directionally solidified columnar nickel-base superalloys (DS alloys). In this project the main theme was, of course, the development of an advanced gas turbine and the alloy developmental work started in 1978 and ended in fiscal 1984. "Advanced Alloys with Controlled Crystalline Structures" was the second project and three types of nickel-base superalloys were treated; they are single crystal alloys (SC alloys), superplastically forgeable P/M alloys, and oxide dispersion strengthened alloys(ODS alloys). This second project was carried out from 1981 to fiscal 1988.

National Research Institute for Metals designed alloys and proposed them as candidate alloys for process studies, which were chiefly carried out by companies participating in the two projects. More precisely, those companies performed their works as members of the especially established organizations, 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 took parts in the second project.

In the second project titanium alloys were also developed, in this paper, however, this subject will not be described.

### Alloy Design:

The present author and his collaborators developed a computeraided alloy design method for gamma/gamma-prime type nickel-base alloys(1) and later a revised version was reported(2). The essential

part of these alloy design programs is made up of giving pairs of gamma and gamma-prime phase compositions in multi-component systems. Many pairs of analysed compositions of gamma and gamma-prime phase compositions were utilized to express phase relations. From the calculated phase compositions, by giving an arbitrary phase volume fraction, one can obtain an alloy composition together with some other factors for the alloy such as lattice parameters of the phases, lattice mismatch, density, creep rupture life, hot corrosion resistance, solution window, etc. The first version relied upon chemically analyzed phase compositions and the second utilized EPMA analysis values of the phases.

### Conventionally Cast Alloys:

Many alloys with various gamma prime contents and various Cr concentrations were designed and examined. As a general trend, 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. Alloy TM-321 was proposed for the first stage blade of the Advanced Gas Turbine of the project. This alloy aimed a higher rupture strength at the sacrifice of hot corrosion resistance. The composition of TM-321 is as follows(in mass %).

## TM-321

8.1Cr, 8.2Co, 12.6W, 5.0Al, 0.8Ti, 4.7Ta, 0.9Hf, 0.05Zr, 0.01B, 0.11C

For the second stage nozzle, Alloy TM-269 was proposed, which has a high melting temperature as well as a high strength. The composition of this alloy is as follows(in mass %).

#### TM-269

9.7Cr, 8.9Co, 13.2W, 4.3Al, 0.6Ti, 3.8Ta, 0.8Hf, 0.05Zr, 0.01B,0.11C

Melting stock manufacture was studied by Daido Steel Ltd. Investment casting of air-cooled blades was studied by Mitsubishi Metals Co. Ltd. and air-cooled second stage nozzles by Hitachi Metals Co. Ltd.

Aluminide coating and thermal barrier coating were studied by NRIM and Toshiba Co. Ltd; Y-doped (PVD) aluminide coating (NRIM) and automated plasma spray coating (Toshiba) were developed.

### Directionally Solidified(DS) Alloy:

Grain boundary cracking is reduced in DS alloys due to columnar crystals. Cracking between columnar crystals in the solidification process is, however, a hazard of this type alloy. This is caused, just after the solidification, by expansion stress from a core to make an air-cooled hollow blade. To avoid this problem NRIM controlled gamma-prime contents in DS alloys. Alloy TMD-5 thus designed was proposed by NRIM to the project. The composition of the alloy is as follows(in mass %):

#### TMD-5

5.8Cr, 9.5Co, 13.7W, 4.6Al, 0.9Ti, 3.3Ta, 1.4Hf, 0.015Zr, 0.015B, 0.07C

Daido Steel Co. Ltd. again prepared melting stocks of this alloy. IHI studied manufacturing hollow DS blades and also took part in determining TMD-5 composition.

#### Single Crystal Alloy(SC):

The target for SC alloy was as follows:

Rupture life at 1040 C and 14 kgf/sq. mm; more than 1000 h. Rupture elongation for the same condition as above; more than 10%.

NRIM applied their alloy design program modified to SC alloys. Various factors such as gamma-prime volume fraction, lattice mismatch of gamma and gamma-prime phases, W/Ta ratio in gamma-prime, solid solutioning degree of gamma-prime, and solution treatment temperature allowance(window). Some typical alloys developed are TMS-1, TMS-12, and TMS-26. The composition of TMS-26, the second proposal alloy for the project is as follows(in mass %):

### TMS-26

### 5.6Cr, 8.2Co, 1.8Mo, 10.9W, 5.1Al, 7.7Ta

Near at the end of the project, the second version of alloy design program was developed, in which many pairs of gamma and gammaprime 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 show long creep rupture strengths. Experiments showed that this was true but unfortunately they gave small elongation values; some modifications to improve ductility will be done.

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

Making good cores is one of the important technologies for single crystal hollow blades. This was investigated by Government Industrial Research Institute, Nagoya. Cores must be held in molten half an alloy for about 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 is not the highest heat resistant ceramics. The main remedies adopted using fused silica of appropiate powder sizes, were 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 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, Hitachi, Ltd., and Hitachi Metals, Ltd. did experiments for producing SC blades and evaluating them. Plasma beam skull remelting was applied to an experimental SC making furnace to minimize the contamination during remelting of the melting stock. To another experimental furnace was applied a static magnetic field to reduce convection. This was expected to be effective for better SC qualities, but the result was not as expected.

Solidification simulation models were used to analyze temperature distribution during solidification. Flat solidification front is required to make an article made up of a single crystal; 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; recrystallization at edges for the alloys and deformation for the cores were sometimes observed.

Superplastically Workable Ni-base Superalloys:

The target for this type alloy in the project was as follows. The UTS at 760 C is more than 160 kgf/sq.mm, tensile elongation at that temperature is more than 20 %, and the alloy must be superplastically forged at around 1050 C. 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. 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 powders without extrusion.

For the alloy design, the above described alloy design program was applied to calculate gamma and gamma-prime 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 but with the calculated compositions of the two phases. An alloy, TMP-3 designed to have a gamma-prime content a little higher than the one in the original alloy showed better superplasticity than that of the original. NRIM proposed this as an official candidate alloy for the process research works, though the alloy does 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. Stronger alloys were developed. An improved version of alloy design program was then developed, and this showed that there would exist still higher strengths, which, however, could not reach the target values.

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. The first one is rather conventional but the second proved to require much research work. 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 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. 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.

Electric Industries, Ltd. treated powders in Sumitomo an attritor to give them strain. The strain induced in powders was expected to promote recrystallizaton 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 can be 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 melt spinning method. Those ribbons showed superplasticity and were used as inserts for diffusion bonding of cast superalloys.

### Oxide Dispersion Strengthened(ODS) Ni-base Superalloys

ODS alloys, made up of gamma, gamma-prime and yittria 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 applied to make ODS blades.

NRIM again proposed a candidate alloy; this was named TMO-2. A previously developed conventionally cast alloy, TM-220, which is one of the strongest alloys, was modified by the alloy design method to get TMO-2. The composition of TMO-2 is as follows(in mass %).

# 5.9Cr, 9.7Co, 12.4W, 4.2Al, 0.8Ti, 4.7Ta, 0.05Zr, 0.01B,

0.05C, 1.1yittria

This alloy, compared to MA 6000 is higher in W and gamma prime contents.

The target for ODS alloy was as follows:

Rupture life at 1100 C and 14kg/sq.mm; more than 1000h. Rupture elongation at that condition; more than 5%.

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

NRIM improved intermediate temperature strength of this type alloy by further increasing gamma-prime content of TMO-2, to get, for instance, TMO-20 which was designed to have a gamma-prime content of 75%.

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

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

Kobe Steel, Ltd. forged isothermally TMO-2 bar to give crude blade shapes. 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 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. 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 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.

### Concluding Remarks and Acknowledgements

Fig.1 shows temperature capabilities of developed alloys together with those of some reference alloys. Fig.2 shows CC, DS, and SC hollow blades cast by some of the participating companies using developed alloys.

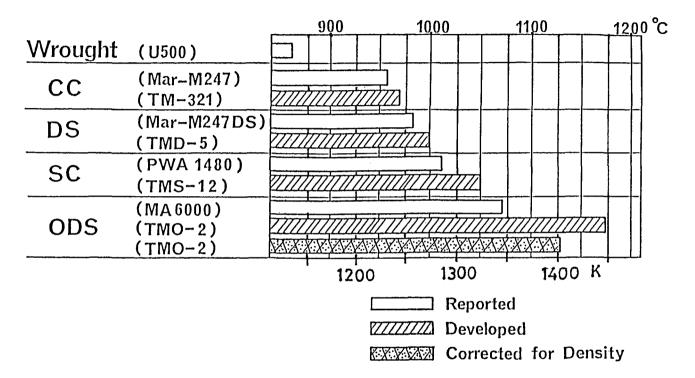


Fig.1 Temperature capability to give a 1000 h rupture life at 14 kg/sq.mm (137.3 Mpa) for Ni-base superalloys.

CC: Conventionally cast alloy, DS: Directionally solidified alloy,

SC: Single crystal alloy, and ODS: Oxide dispersion strengthened alloy.

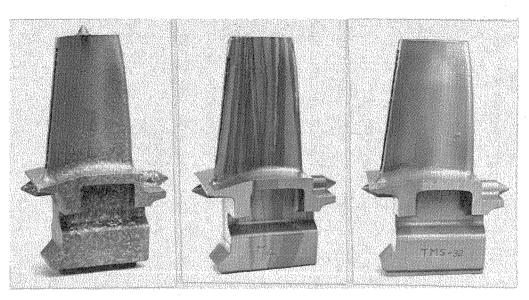


Fig.2 CC blade, DS blade, and SC blade (from left to right);all air-cooled hollow blades made using alloys developed by NRIM. Casting by Komatsu-Howmet, Ltd.(CC) and by IHI (DS and SC).

A symposium was held in March of 1989 for "Advanced Alloys with Controlled Crystalline Structures". All the participating<sup>®</sup> organizations talked their results in the Symposium and the present paper, for the latter half, largely depends on the Proceedings of that Symposium(3).

#### References

(1) H.Harada and M.Yamazaki: Tetsu-to-Hagane, 65(1977), 1059,

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(3) Proceedings of 6th Symposium for "Advanced Alloys with Controlled Crystalline Structures", held in Tokyo, 23-24 March, 1989.