PHASE CALCULATION AND ITS USE

IN ALLOY DESIGN PROGRAM FOR NICKEL-BASE SUPERALLOYS

H. Harada, K. Ohno, T. Yamagata,
T. Yokokawa, and M. Yamazaki

National Research Institute for Metals
2-3-12 Nakameguro, Meguro-ku, Tokyo 153, Japan

Abstract

A series of phase calculation equations for γ and γ' phases in nickel-base superalloys was established by regression analysis on the EPMA data obtained from 30 experimental or commercial alloys together with data from a Ni-Al binary phase diagram. By using these equations, an accurate calculation of γ/γ' equilibrium, at 900°C, was made possible for various compositions of alloys, from Ni-Al binary to Ni-Co-Cr-Mo-W-Al-Ti-Nb-Ta-Hf-Re multi-component alloys. These phase calculation equations were substituted for those having been used in our alloy design program to extend the applicable composition range and to improve the accuracy of phase and property calculations of the program. Furthermore, a calculation equation for creep rupture life of SC alloys was established and adapted to the program. Using this new version of alloy design, the phase and property were successfully calculated for various types of γ' precipitation hardening nickel-base superalloys.

Superalloys 1988
Edited by S. Reichman, D.N. Duhl,
G. Maurer, S. Antolovich and C. Lund
The Metallurgical Society, 1988

Introduction

In the design of γ' precipitation hardening nickel-base superalloys, it is of prime importance to calculate the compositions and fractions of γ and γ' phases at high temperatures with a high accuracy, not only for the prediction of the formation of undesirable phases but also for the further calculations of high temperature properties of the alloys.

Some of the authors previously developed an alloy design program for γ' precipitation hardening nickel-base superalloys [1,2]. By this program, calculations were made possible for γ/γ' phase equilibrium as well as other structural parameters (e.g., lattice misfit values). Furthermore, high temperature properties, such as creep rupture life and high corrosion resistance, could also be calculated by this program. This program has been successfully applied to the development of conventionally cast (CC), directionally solidified (DS), single crystal (SC), powder metallurgical (PM), and oxide dispersion strengthened (ODS) alloys in national projects of Japan [2-6]. However, this program still had a limitation in the applicable composition range. For instance, the phase calculation was not possible for some existing alloys, such as Alloy 454. This could be attributed to the data for γ and γ' compositions [7,8] on which our phase calculation equations were established; the compositions were obtained from alloys with various heat treatments and, in addition, the alloy compositions were not widely distributed in the γ/γ' two phase region. Both of these prevented us from establishing very accurate phase calculation equations between the two phases at high temperature.

This study was performed to reconstruct our alloy design program using our own careful EPMA analysis on experimental and commercial alloy specimens having various compositions which were aged for long times at temperature.

Experimental

Specimens of 20 experimental and 10 commercial alloys, including CC, DS, and SC alloys, were heated at 1100 to 1175°C for 30 hrs after cold work so that γ/γ' two phase recrystallization occurred to form a coarse γ/γ' structure. The specimens were then slowly cooled from these temperatures to 900°C and aged for 1500 hrs in order to achieve the equilibrium state at 900°C followed by water quenching.

The specimens thus heat-treated had γ/γ' lamellar or γ' rod/γ structures of 3 to 5 microns thickness in both phases. These structures were coarse enough to be analyzed by EPMA with a high accuracy. On the 30 pairs of thus analyzed γ and γ' compositions together with a pair from Ni-Al binary phase diagram, regression analysis was carried out to establish the phase calculation equations. A series of equations obtained were substituted for those having been used in our alloy design program to improve accuracy and extend applicable composition range of the program. Furthermore, the calculation of creep rupture life of properly heat-treated SC alloys was made possible on the basis of this phase calculation.

Phase Calculation

The $\gamma+\gamma'$ region in multi-component nickel-base superalloys is presented schematically in Fig. 1. The γ' hypersurface in this figure, on which compositions of γ' equilibrated to γ should be lying, could be expre-

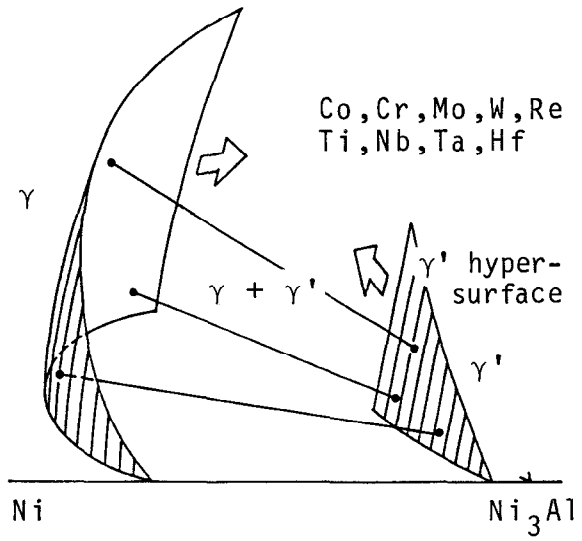

Fig. 1. Schematic phase diagram of multi-component nickel-base superalloys.

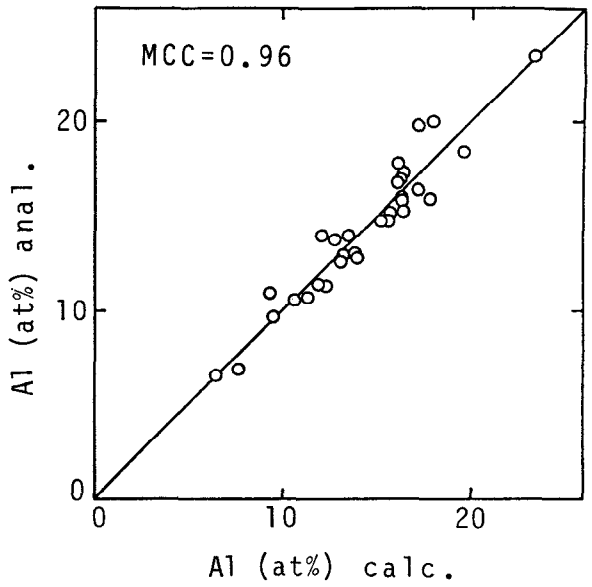

Fig. 2. Relationship between analyzed and calculated Al concentrations in γ'phase.

ssed by a regression equation, eq.1, where X'_i is a concentration of i-th element in γ'phase.

$$X'_{Al} = 23.4 - 0.03 \cdot X'_{Co} - 0.55 \cdot X'_{Cr} - 0.71 \cdot X'_{Mo} - 0.74 \cdot X'_{W} - 0.86 \cdot X'_{Ti} - 0.96 \cdot X'_{Nb} - 0.48 \cdot X'_{Ta} - 1.08 \cdot X'_{Hf} (-0.74 \cdot X'_{Re}) \quad \text{-------- (1)}$$

For this regression analysis, the 30 analyzed γ'compositions were used together with a γ'composition from Ni-Al binary phase diagram at 900 °C[9]. Since the number of alloys containing Re was too small to give a confident coefficient value, the same value as W was used for Re. MCC(Multiple Correlation Coefficient) of the equation was 0.96. Although this value was slightly smaller than that of the equation in our previous paper, the value being 0.98, the applicable composition range was found to be remarkably extended. Fig. 2 shows a good agreement between calculated(by eq.1) and analyzed Al concentrations in the γ' phase. The agreement holds in a wide range, from 23.4 at% (in Ni-Al binary alloy) to 6.5 at% (in highly solid solutioned multi-component alloy), whereas the previous equation derived from the data in literature[7,8] tended to give significant amount of error when it was used in a composition range of Ni-Al binary and near to it.

In order to calculate the composition of γ which is equilibrated to a γ' on the γ'hypersurface, partitioning ratios defined as $R_i=X_i/X'_i$, where X_i is a concentration of i-th element in γ phase, are needed. Those of Co, Cr, W, and Al could be well expressed by regression analysis on the 31 pairs of γ and γ'compositions, as functions of the γ'composition, eqs. 2, 3, 4, and 5. The MCCs were 0.98, 0.92, 0.89, and 0.83, in order. They were increased by 0.07 to 0.13 compared with those in our previous work[2], except W, a

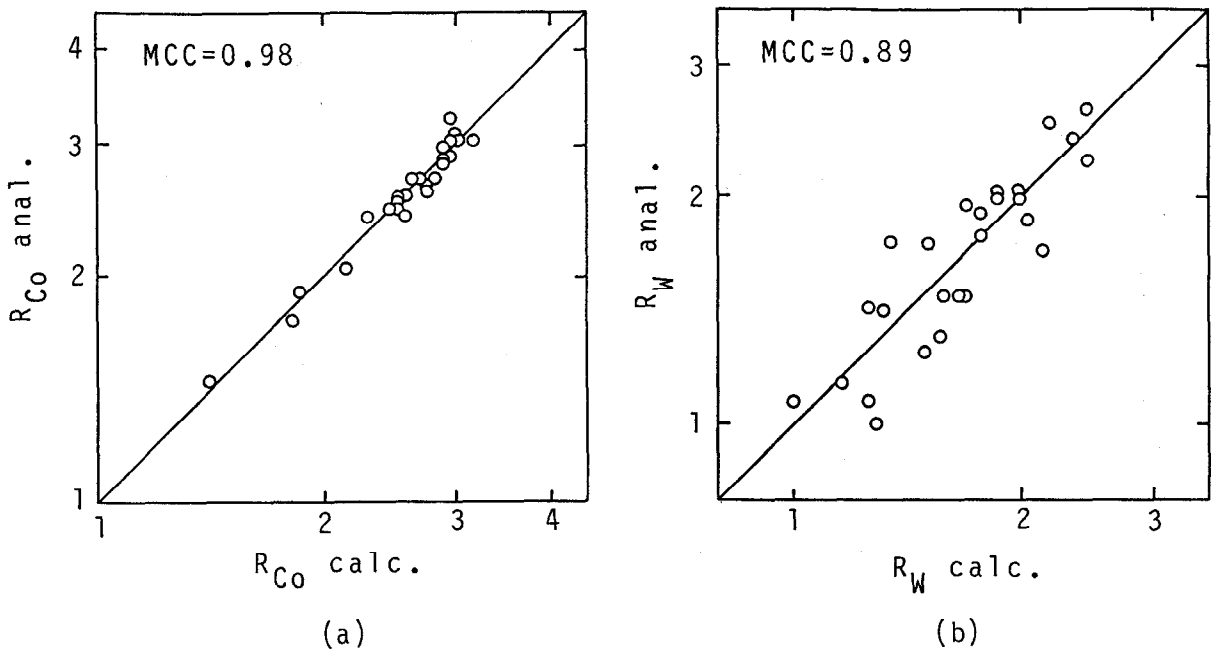

Fig. 3. Relationship between analyzed and calculated partitioning ratios for Co (a) and W (b).

constant value having been used for it. Partitioning ratios of other elements were found to be well expressed as constants, R_{Mo}=3.93, R_{Ti}=0.18, R_{Nb}=0.30, R_{Ta}=0.22, R_{Hf}=0.15, and R_{Re}=10.6.

$$\log_{10}(R_{Co}) = 0.529 - 0.012 \cdot X'_{Co} - 0.012 \cdot X'_{Cr} - 0.008 \cdot X'_{W} + 0.005\, X'_{Ti} \quad \text{---------- (2)}$$

$$\log_{10}(R_{Cr}) = 1.429 - 0.009 \cdot X'_{Co} - 0.061 \cdot X'_{Cr} - 0.103 \cdot X'_{Mo} - 0.033 \cdot X'_{W} - 0.016 \cdot X'_{Al} \quad \text{---------- (3)}$$

$$\log_{10}(R_{W}) = -0.141 - 0.015 \cdot X'_{Co} + 0.052 \cdot X'_{W} + 0.037 \cdot X'_{Ti} + 0.085 \cdot X'_{Nb} + 0.077 \cdot X'_{Ta} \quad \text{---------- (4)}$$

$$\log_{10}(R_{Al}) = -0.274 + 0.013 \cdot X'_{Co} - 0.058 \cdot X'_{Mo} - 0.073 \cdot X'_{W} - 0.023 \cdot X'_{Ti} - 0.087 \cdot X'_{Nb} - 0.057 \cdot X'_{Ta} \quad \text{--------- (5)}$$

Fig. 3(a) shows a good agreement between analyzed and calculated (by eq. 2) partitioning ratios of Co; analyzed ones, distributed from 1.5 to 3, are perfectly expressed by the calculation. In case of W, as shown in Fig. 3(b), the agreement is not as good as with Co, but the equation still expresses the partitioning behavior, the values being distributed from 1 to 2.5. Obviously, using these four equations together with the constant values, the error in phase calculation is expected to be minimized. This is in contrast to PHACOMP [10] where using constant values for all the partitioning ratios to calculate the γ and γ' compositions could give a significant amount of error in the result.

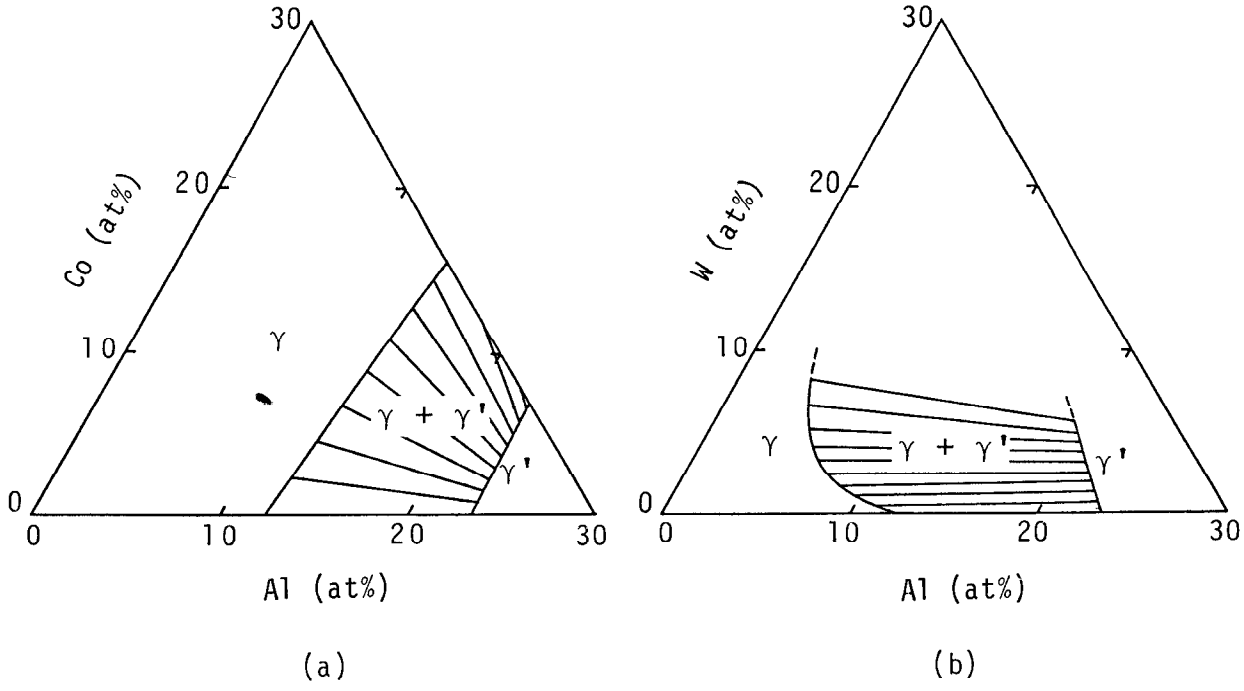

Fig. 4. Calculated $\gamma + \gamma'$ region with tie-lines, at 900°C, for Ni-Al-Co (a) and Ni-Al-W (b) ternary systems.

By substituting the phase calculation equations thus obtained for those having been used in our alloy design program, the effective range of the program was remarkably extended; this new version could be applied to almost all the γ/γ' two phase composition range, from Ni-Al binary to Ni-Co-Cr-Mo-W-Al-Ti-Nb-Ta-Hf-Re multi-component systems.

The γ/γ' equilibrium in Ni-Al-X ternary systems, X= Co, Cr, Mo, W, Ti, Nb, Ta, and Hf, at 900°C, could be successfully calculated by the phase calculation equations. Fig.4 (a) shows the calculation for Ni-Al-Co ternary system. The $\gamma+\gamma'$ region calculated was very consistent with phase diagrams at 800, 1000, and 1200°C available from literature[11]. In Ni-Al-W ternary system, the $\gamma+\gamma'$ region calculated and shown in Fig. 4 (b) was again very consistent with an available phase diagram at 1250°C[12], tie-lines being not shown in it.

In multi-component alloys, a very good agreement was observed between calculated and analyzed chemical compositions of γ and γ' phases, examples being shown in Table I. The first four alloys in the table are alloys included in the 30 alloys used for EPMA analysis and so the agreement in these alloys indicates a good 'interpolation' of the phase calculation. It is to be noted that the calculation for Alloy 454, which was not possible by the old version, becomes possible here. The agreement observed in the last four alloys, whose analyzed data were not used to establish phase calculation equations, indicates a very good 'extrapolation' of the phase calculation in multi-component systems.

From all of these examinations, it was concluded that the γ/γ' phase equilibrium at 900°C could be calculated by our phase calculation equations with a very high accuracy, for almost all the γ/γ' two phase composition range, from Ni-Al binary to multi-component alloys.

Table I. Comparison between calculated and analyzed chemical compositions of γ and γ' phases, at 900 °C, with atomic fractions (f) of γ' phase calculated from the compositions.

Alloy	Phase	Chemical composition (at%)									f
		Co	Cr	Mo	W	Al	Ti	Nb	Ta	Hf	
IN738LC	calc. γ'	3.8	3.1	0.4	0.5	13.0	7.7	0.9	0.9	-	0.41
	γ	11.4	26.8	1.4	1.0	3.4	1.3	0.3	0.2	-	
	anal. γ'	3.8	3.3	0.3	0.5	12.9	7.4	0.9	0.9	-	0.42
	γ	11.7	27.2	1.5	0.9	3.2	1.4	0.3	0.2	-	
B1900Hf	calc. γ'	5.5	2.7	1.4	-	18.1	1.3	-	1.8	0.6	0.54
	γ	14.9	15.9	5.6	-	7.0	0.2	-	0.4	0.1	
	anal. γ'	5.4	3.4	2.2	-	19.7	1.2	-	1.8	0.6	0.52
	γ	14.8	14.8	4.7	-	5.5	0.3	-	0.4	0.1	
MM247DS	calc. γ'	6.8	3.2	0.2	2.9	16.6	1.6	-	1.1	0.6	0.64
	γ	16.8	19.7	0.6	3.2	5.2	0.3	-	0.3	0.1	
	anal. γ'	6.4	3.3	0.2	2.8	17.3	1.7	-	1.2	0.6	0.59
	γ	16.2	17.5	0.5	3.2	5.5	0.4	-	0.3	0.1	
ALLOY 454	calc. γ'	3.1	3.2	-	0.9	15.8	2.7	-	5.6	-	0.64
	γ	8.8	26.5	-	2.1	3.3	0.5	-	1.3	-	
	anal. γ'	2.9	3.1	-	0.8	16.8	2.7	-	5.3	-	0.59
	γ	8.2	23.6	-	2.0	3.3	0.7	-	1.4	-	
CMSX-2	calc. γ'	2.7	2.7	0.2	2.1	17.4	1.7	-	2.7	-	0.61
	γ	7.8	19.6	0.7	3.3	4.4	0.3	-	0.6	-	
	* anal. γ'	3.2	2.4	0.2	2.4	16.7	1.6	-	3.0	-	*** 0.68
	γ	n.d.									
MXON	calc. γ'	3.4	4.0	0.7	2.4	17.6	-	-	2.6	-	0.69
	γ	8.9	20.9	2.6	3.2	4.5	-	-	0.6	-	
	** anal. γ'	3.0	2.7	0.7	2.7	17.9	-	-	2.5	-	*** 0.69
	γ	n.d.									
TM-53	calc. γ'	5.1	2.9	-	2.0	13.0	7.7	-	1.1	-	0.67
	γ	14.5	24.3	-	3.7	3.3	1.4	-	0.3	-	
	anal. γ'	5.6	3.5	-	1.6	11.5	7.6	-	1.2	-	0.66
	γ	13.6	26.5	-	4.2	3.1	1.5	-	0.2	-	
TMS-1	calc. γ'	5.2	2.3	-	4.7	17.3	-	-	2.5	-	0.64
	γ	13.2	14.6	-	7.7	3.6	-	-	0.6	-	
	anal. γ'	5.5	2.6	-	5.0	16.2	-	-	2.4	-	0.68
	γ	13.6	15.5	-	7.4	3.9	-	-	0.6	-	

* at 850 °C [13], ** at 850 °C [14], *** Wt. fraction

Table II. Some of the structural parameters and properties calculated by the new version of alloy design program.

Alloy	γ' atomic fraction	Lattice misfit (%)	Density (g/cm^3)	Creep rup.life(h) *CC	**SC	***Hot corrosion rate
			CC alloys			
Inconel713C	0.55	-0.21	7.96	51	-	8.3
IN 738LC	0.41	0.23	8.21	24	-	1
B1900Hf	0.54	-0.07	8.21	189	-	2.4
MarM200	0.61	0.08	8.50	298	-	2.3
TM-321	0.61	0.21	8.82	767	-	1.5
			DS alloys			
MarM247DS	0.64	0.17	8.57	(688)	-	0.7
Rene 125	0.63	0.14	8.51	(533)	-	0.4
TMD-5	0.59	0.19	8.96	(1094)	-	1.4
			SC alloys			
Alloy 454	0.64	0.58	8.68	(591)	209	(3.6)
NASAIR100	0.72	-0.13	8.59	(551)	420	(4.1)
SRR 99	0.67	0.12	8.50	(505)	367	(1.9)
RR2000	0.57	-0.02	7.90	(99)	181	(0.8)
Rene N4	0.56	0.39	8.51	(249)	52	(1.2)
CMSX-2	0.61	0.29	8.61	(496)	763	(4.6)
MXON	0.69	0.01	8.62	(626)	728	(9.1)
MMT143	0.60	-0.38	8.61	(930)	>10000	(188.5)
TMS- 1	0.64	0.16	9.16	(1492)	1747	(8.9)
TMS-12	0.60	0.33	9.06	(894)	3486	(10.5)
SC 83	0.55	0.18	8.84	(498)	2168	(21.2)
			PM alloys			
MERL 76	0.49	0.20	8.05	(50)	-	0.6
Rene 95	0.48	0.04	8.26	(31)	-	5.3
AF 115	0.60	0.01	8.34	(158)	-	0.8
TMP-3	0.57	0.16	8.26	(75)	-	6.3
			ODS alloys(Base metal)			
MA 6000	0.49	-0.03	8.21	(63)	-	1.6
TMO-2	0.47	0.30	8.98	(281)	-	8.3

* at 1000°C-118MPa, assuming CC structure, grain size about 3 mm.

** at 1040°C-137MPa, assuming solutioned and aged SC structure, tensile axis within 10° of <100>.

***Penetration depth in burner rig test at 850°C, normalized by IN738LC(=1).

Calculations of other structural parameters, as well as high temperature properties, were made possible on the basis of the phase calculation mentioned above. The calculation equations established in our previous paper could be successfully used for this purpose after a little modification. The structural parameters and properties thus calculated were / density / solubility index(our criterion of phase stability) / PHACOMP parameters / lattice parameters and misfit(at room temperature) / liquidus-solidus temperatures / creep rupture strength(for CC) / tensile properties(for CC, at 900°C) / hot corrosion resistance(in crucible test at 900°C and burner rig test at 850°C) / and so on.

In addition to these calculations, a calculation of creep rupture life of SC alloys, at 1040°C and at 137MPa, became possible by a regression equation, as a function of γ'composition, γ'at. fraction, and γ/γ'lattice misfit. The MCC of the equation was 0.91 when the analysis was carried out using data from our experimental alloys which were cast, heat-treated, and tested in a unified condition. When the data from 6 commercial or experimental alloys in literature were used together with ours, the MCC reduced to 0.84. This was probably because of the difference in heat treatment conditions, which will be taken into account in the equation.

It was remarked in both equations that the effect of the lattice misfit, as well as other factors, was found to be very large. The coefficients of the lattice misfit in the equations suggested that the rupture life became longer by factor of 2 or more per every 0.1% change of lattice misfit toward negative($a_{\gamma'} < a_{\gamma}$), e.g., from +0.3% to +0.2%. This strongly supported the effect of large negative lattice misfit on the formation of rafted structure which increased the creep resistance. Because almost all the alloys used for the regression analysis were expected to have negative lattice misfit values at high temperatures such as 1040°C, the change toward negative at room temperature was very likely to correspond to a change toward larger negative lattice misfit in the negative range at 1040°C.

```
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)  LIFE.CC(H)
 0.596     3.594    2.325   1411.4   1354.4  5863.47    477.4     893.6

 DENSITY  LAT.G(A)  NV.G   SOL1(C)  SOLV(C)   H.COR.B UTS(MPA) LIFE.SC(H)
 9.062     3.582    1.870   1396.3   1309.3     10.48    556.3    3485.8

 SI       LM(%)   NV.G-NVC RANGE(C) WDW (C)          EL(%)   SPC.STRGTH
 1.163    0.327    0.197      15.1     45.1             6.8     15.689
**********************************************************************
 TRY AGAIN ?  < YES(0) NO(1) >
```

Fig. 5. Output of 'Phase & Property' calculation, for alloy TMS-12, by the new version of alloy design program.

The calculation equation for creep rupture life of SC alloys having MCC of 0.84 was adapted to the alloy design program. Calculation equations for solidus and solvus temperatures were also established on microstructure observation data as functions of the alloy composition, and this was also adapted to the program. An example of the phase & property calculation by this new version of alloy design program is shown in Fig. 5, for Alloy TMS-12, a single crystal alloy developed by the authors using the previous alloy design program.

The calculation was successfully made for various currently used and recently developed alloys, including CC, DS, SC, PM, and ODS alloys. Some of the results are shown in Table II. In the table, TM-321, TMD-5, TMS-1,12, TMP-3, and TMO-2 are alloys designed by authors using previous alloy design program. Alloy SC 83 was designed by Ohno and Watanabe[15], the actual creep rupture life being 3100 hrs at this testing condition. In some SC alloys, the actual creep rupture life was longer than the calculation, probably because of the optimum heat treatments performed for the alloys; MXON, for example, had a life of 1500hrs. It is to be noted here that alloy MMT-143 is calculated to have very long rupture life mainly because of the large negative lattice misfit, although the calculation is effective so far as the misfit dislocation is not formed before testing.

Application of the Alloy Design Program

This new version of alloy design program will be used for alloy developments of various types of γ' precipitation hardening nickel-base superalloys, especially the SC alloys, using the calculation equation of creep rupture life as well as all the other calculation equations.

This new version can also be used for quality control of various types of alloys during processing. For example, it is possible to calculate the 'Phase and Property' from the check analysis before tapping the molten metal to make remelt bars or castings and, if needed, one could adjust the chemical composition so that the alloy could exhibit the needed high temperature properties.

Conclusions

1. A series of phase calculation equations for γ and γ' phases in nickel-base superalloys was established by regression analysis on our EPMA data from 30 experimental or commercial alloys and a data from Ni-Al binary phase diagram.
2. An accurate calculation of γ/γ' equilibrium, at 900°C, was made possible by using these equations for various compositions of alloys, from Ni-Al binary to Ni-Co-Cr-Mo-W-Re-Al-Ti-Nb-Ta-Hf multi-component alloys.
3. A calculation equation for creep rupture life of SC alloys, revealing the strong effect of lattice misfit, could be obtained on the phase calculation and adapted to our alloy design program.
4. Using this new version of alloy design program, phase and property calculation was successfully carried out for various types of γ' precipitation hardening nickel-base superalloys.

Acknowledgment

This work was performed as a part of the R&D project of Basic Technology for Future Industries sponsored by Agency of Industrial Science and Technology, MITI.

References

[1] H.Harada and M.Yamazaki;Tetsu-to-Hagane,65(7)(1979),p.1059(written in Japanese).

[2] H.Harada, M.Yamazaki, Y.Koizumi, N.Sakuma, N.Furuya, and H.Kamiya; Proc. of Conference, High Temperature Alloys for Gas Turbines 1982 , held in Liege, Belgium, 4-6 Oct. 1982, D.Reidel Publishing Co, p.721.

[3] T.Yamagata, H.Harada, S.Nakazawa, M.Yamazaki, and Y.G.Nakagawa; presented at Conference, "5th international symposium on Superalloys", held at Seven Springs, Pa, U.S.A., 7-11 Oct. 1984(Proceedings: Superalloys 1984, published by the Metallurgical Society of AIME,p157)

[4] M.Yamazaki; Progress in Powder Metallurgy, vol.41(1986),p.531.

[5] T.Yamagata, H.Harada, S.Nakazawa, and M.Yamazaki; Trans. Iron and Steel Inst.of Japan, vol.26,(1986),p.638.

[6] T.Yamagata, H.Harada, and M.Yamazaki: Proc. of Conference "The 1987 Tokyo International Gas Turbine Congress", held in Tokyo, Japan, 26-31 Oct. 1987, sponsored by Gas Turbine Society of Japan, vol 3, p.239.

[7] O.H.Kriege and J.M.Baris: Trans. ASM, vol.62(1967),p.195.

[8] J.E.Restall and E.C.Toulson: Metals and Materials, March(1973),p.134, April,p.187.(Part 1 and 2).

[9] Constitution of Binary Alloys, 2nd Ed. by M.Hansen and K.Anderko, McGrow-Hill, New York, 1958. p.119.

[10] R.F.Decker: Symposium on Steel Strengthening Mechanisms, Climax Molybdenum Company, May 1969,Greenwich, Connecticut, U.S.A.,p.147.

[11] J.Schramm, Z.Metallk. vol.33(1941) p.403.

[12] P.Nash, S.Fielding, and D.R.F.West: Met. Sci.,vol.17(1983),p.194.

[13] P.Caron and T.Khan: Mat. Sci. and Engineering, vol.61(1983),p.173.

[14] T.Khan, P.Caron and C.Duret: presented at Conference, "5th international symposium on Superalloys", held at Seven Springs, Pa, U.S.A., 7-11 Oct. 1984(Proceedings: Superalloys 1984, published by the Metallurgical Society of AIME,p.145).

[15] T.Ohno and R.Watanabe: Tetsu to Hagane, vol.72, No.13(1986), S1509(written in Japanese).