A GENERAL METHOD FOR THE PREDICTION
OF PRECIPITATE COMPOSITIONS

J. S. Slaney

Abstract

The shortcomings of present methods of prediction are considered and a
new method is proposed. This is based upon the maximum solubility of
individual elements in the precipitating phase and the availability of
such elements in the alloy. The plan of a computer program is suggested
and a comparison made between an analyzed and predicted composition of
gamma prime.

J. S. Slaney is Senior Research Associate with Latrobe Steel Company,
Latrobe, Pennsylvania.

Introduction. Methods of prediction of the formation of phases such as sigma in superalloys, depend upon assumptions regarding the composition of precipitating phases such as carbides, borides and more importantly, the strenghtening phase. After the elements of these phases are removed, the formula given by Beck and his co-workers (1) is applied to the remaining matrix to obtain an average electron-vacancy number. This number is a measure of the propensity of the matrix to form electron compounds. This type of prediction calculation has come to be known by the name PHACOMP.

Discussion. The anomolous behavior of Inconel 713C has been something of a problem when trying to apply the PHACOMP calculations to predict the formation of sigma. Consideration of this problem has led to this proposal for a general method of prediction of precipitating phase composition.

Although a safe number has been developed for some super alloys, it has frequently been found that alloys in the 713 range, while calculating to a low and supposedly-safe number, will in fact form sigma on long-time exposure at temperature. This effect has been well documented in the work being done by Collins and Kortovich at TRW on an Air Force contract (2). In this contract work, the method most successful in dealing with 713C has been that using the composition of gamma-prime due to Dreshfield which is taken to be

$$Ni_{2.95}(Mo+W)_{.05}(Ti+Al+Ta+Cb+Zr+0.5\ V+0.3\ Cr)$$
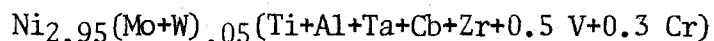
this being the composition of the gamma-prime which he found in the alloy TAZ8B. The figures in front of vanadium and chromium are that proportion of the total atomic percentage of the element present in the alloy. Although calculations, based on the use of this composition for gamma-prime have been more successful than others, in 713C at any rate, this is not the composition one might expect from Guard and Westbrook's work on the nickel-aluminum system (3). Their phase diagram, Fig. 1, for approximately 2100°F shows cobalt and copper substituting almost exclusively on the nickel side of Ni_3Al; titanium, silicon, vanadium and manganese on the aluminum side and about 50/50 partition of iron, chromium and molybdenum between the two sides. Decker and Bieber's work on 713C (4) has indicated that nearly all of the columbium goes into the aluminum side while Arbusov (5) shows tungsten on both sides.

The Guard and Westbrook phase diagram for Ni_3Al gives a clue as to the reason for the difficulty with 713C. Their diagram shows that cobalt substitutes on the nickel side almost exclusively. Now, at the time the original calculations concerned with sigma control in Udimet 700 were made (6), there was no chemically-analyzed composition of gamma-prime available other than that given by Decker and Bieber in their work on 713C - which contains no cobalt. Consequently, the assumption was made that the gamma-prime in Udimet 700 also contained no cobalt, whereas there must have been a considerable amount in it since this alloy contained about 18% of this element. This omission was repeated in other assumed compositions for gamma-prime (7). Now, because

the number given by Beck and his co-workers was found to be much too high for this control work, the electron-vacancy number for a similar alloy was used as a target figure. This alloy was a Udimet 500 heat known to be sigma free. At this point it should be pointed out that when Beck gave his range of numbers for the formation of sigma he was referring to the single phase region (sigma) whereas of course, we here are concerned with the two-phase (gamma plus sigma) region, which must be associated with a much wider range of electron vacancy numbers.

To return to the present argument, it will be noted that the sigma-free Udimet 500 alloy used for a target figure was also an alloy which contained a lot of cobalt. The consequence was that the same error was repeated in the Udimet 500 target calculation and the Udimet 700 control calculation; thus, the two errors cancelled each other. However, when the calculation was applied to 713C alloy, we had the built-in error from the Udimet 500 calculation but no error in the 713C calculation because the composition of the gamma-prime was now more nearly correct, and the error was not cancelled.

Effect of Cobalt in The Sigma Calculation. Since the cobalt substitutes for nickel, it does not improverish the matrix in nickel, but where it is present in an alloy, it will be removed from the matrix by the precipitation reaction. The consequence of this is that it will actually be less effective in forming sigma although in the old method it will be calculated as being more effective than it is. Notice that this will tend to rate the number relatively higher -- hence more sigma prone -- in a cobalt-containing alloy and relatively lower -- hence safer -- in a lower-cobalt alloy. Thus, it will be seen that 713C alloy will calculate to a low and safe number when in fact it will likely form sigma; and this is known to be the case.

It should be noted that this effect will only be seen when the alloy matrix is near to the critical gamma-gamma+sigma boundary as is the case with 713C. For instance, there are several cobalt-free alloys in the work being done at TRW which do not form sigma; however, these alloys are so far away from the sigma boundary that they do not form sigma anyway and the error does not show up.

These considerations lead to a type of calculation which should have quite general application. Given below are the outlines of such a calculation.

Assumptions Used in The Calculation. It should be noted that the numbers which are mentioned in this section can be changed if necessary as is shown in the appendix.

Carbides

1. If molybednum plus tungsten atomic percent is more than 3.5, then M_6C is formed to reduce the residual molybdenum plus tungsten to less than 3.5 atom percent.

2. If columbium and/or tantalum are present at more than .4 atom percent, the carbon forms MC.

3. If less than .4 atom percent of columbium and/or tantalum is present, half the carbon goes to form MC and half goes to $M_{23}C_6$. As mentioned above, provision is made for these to vary in a proposed computer program.

Borides

Assume all of the boron forms M_3B_2 of composition Mo_3B_2.

Gamma Prime

Make the obviously-wrong assumption that after the formation of the carbides, all of the aluminum, titanium, columbium and tantalum form gamma prime. As a first approximation, the percentage of substituting elements in the gamma prime will be given by the maximum solubility of the various elements at the temperature of exposure multiplied by the percentage available in the alloy. For example, the chromium in alloy 713 is 14.45 atom percent. Taylor and Floyd (8) report that chromium solubility in gamma prime at 1562°F is about 16 atom percent. So we might expect 16% X 14.45% which equals 2.32 atom percent in gamma prime. Decker and Bieber in their determinations found 2.25 atom percent. Not a bad correlation. As a matter of fact, the whole of the gamma prime composition for 713C as calculated by this method (Appendix II) compares quite favorably with that determined by Decker and Bieber.

Of course when we speak of the maximum solid solubility we are really referring to the maximum solubility at the temperature at which the alloy is being soaked for a long period of time. We don't have all of this data now but as a first approximation we can use the data such as that of Guard and Westbrook and of Floyd and Taylor. Multiplying the atomic percent of the element in the alloy by its maximum solubility at the nearest temperature we have available, will give the expected approximate composition of the gamma-prime. Later when more precipitate compositions are determined, we could use the known precipitate composition to correct the maximum solid solubility of the element. This is possible if the atomic percentage in the precipitate and the atomic percent of the alloy are known because the maximum solid solubility in atomic percent is equal to the observed atomic percent in the precipitate divided by the atomic percentage available in the alloy.

Calculations. Appendix I lists the assumptions made for this calculation and suggests a possible plan for a computer program. One of the objects of this program would be to have various constants in it so that these could be changed as more accurate information became available. Appendix II is a sample calculation of the variable gamma prime program carried out on 713C alloy. This serves as a check on the prediction method because we have a calculated composition for the gamma prime in

70

this alloy and an observed composition arrived at by chemical means.
The comparison is shown at the end of the appendix and is not too bad.
Appendix III is a calculation for a typical Udimet 700 analysis with a
predicted value for the gamma prime. When this is analyzed in the
future, the accuracy of the prediction (and the assumptions) will be
checked again.

No changes are proposed for the final calculation of electron-
vacancy number in this note, but I believe that a more accurate
prediction of the precipitating phases will lead us to a better idea of
the composition of the matrix from which the sigma forms.

With regard to the final electron-vacancy number, it cannot be
emphasized too strongly that this depends upon the assumptions made in
the calculation and consequently, so does the "safe" number. Therefore
every time an N_V number is quoted, the assumptions made or method used
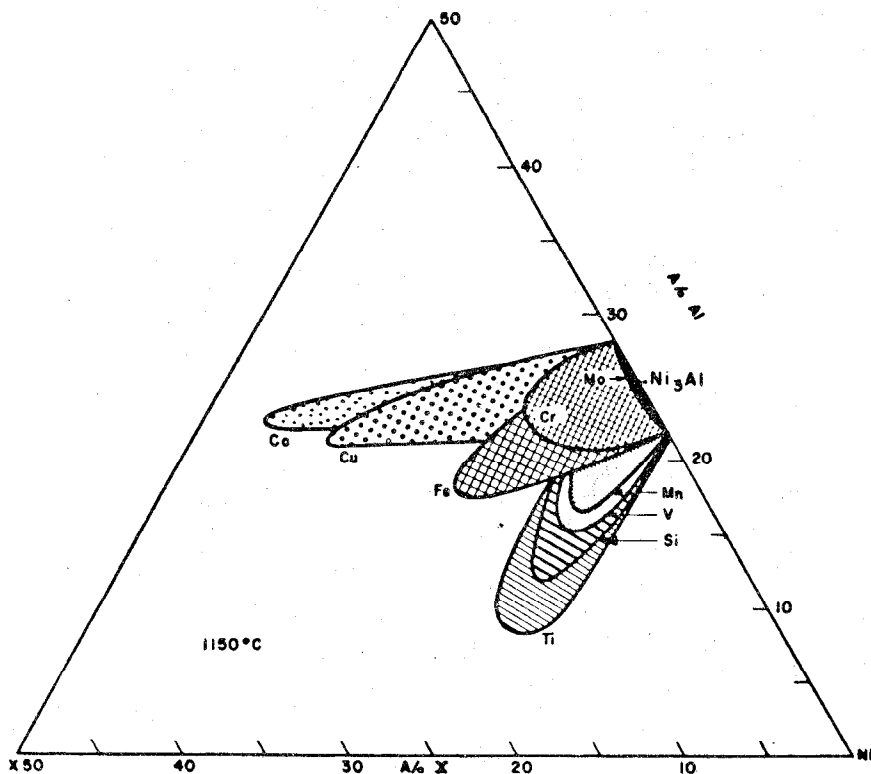to obtain this number should be referenced.

Fig. 1 - Ni₃Al solid - solution field at approximately
2100°F for various ternary alloys. After Guard and
Westbrook (3).

71

REFERENCES

(1) Sheldon Rideout, W. D. Manly, E. L. Kaman, B.S. Lement and
Paul A. Beck: Intermediate Phases in Ternary Alloy Systems of
Transition Elements, pp. 872-876, Journal of Metals, October, 1951.

(2) H. E. Collins and C. S. Kortovich: Research on Microstructural
Instability of Nickel-Base Superalloys. A. F. Contract 33 (615) -
5126.

(3) R. W. Guard and J. H. Westbrook: The Alloying Behavior of Ni_3Al
(Gamma-Prime Phase). Met. Soc. AIME 215, 807 (1959).

(4) R. F. Decker and C. G. Bieber: Microstructure of a Cast Age -
Hardenable Nickel-Chromium Alloy. Symposium on Electron Metallo-
graphy, ASTM Special Technical Publication No. 262.

(5) M. P. Arbuzov, E. T. Kachkovskaya and B. V. Kaenko. Fisika Metallov
i Metalovedenie, 1966, 21, (6), 854-857.

(6) W. J. Boesch and J. S. Slaney. Preventing Sigma Phase Embrittlement
in Nickel-Base Superalloys, Metal Progress, 86, 109, 1964.

(7) L. R. Woodyatt, C. T. Sims and H. J. Beattie, Jr. Prediction of
Sigma-Type Phase Occurrence from Compositions in Austenitic
Superalloys. Transactions, Met. Society AIME 236, 519 (1966).

(8) A. Taylor and R. W. Floyd. The constitution of Nickel-Rich Alloys
of the Nickel-Chromium-Aluminum System. Journal of the Institute
of Metals, pp. 451-464, 81, 1952-53.

Assumptions and Constants for Variable
Gamma-Prime Prediction

Carbides

Assume

1. If Mo + W a/o is more than a a/o, then M_6C of composition d is formed to reduce the Mo + W a/o to a a/o.

2. If Cb + Ta are present at more than b a/o, then all of the C forms MC of composition e.

3. If less than b a/o of Cb + Ta are present, c x C a/o forms MC of composition f and (1-c)xCa/o forms $M_{23}C_6$ of composition g.

Borides

Assume

All of the B forms M_3B_2 of composition a'.

Gamma-Prime

Assume

1. m of Al, n of Ti, o of Cb and p of Ta enter gamma-prime on the Al side.

2. Composition of the gamma-prime is:

$$(Ni_{75-\Sigma Ni_S} + Co_{a/oxh} + \frac{Fe_{a/oxi}}{Z} + \frac{Cr_{a/oxj}}{Z} + \frac{Mo_{a/oxh}}{Z} + \frac{W_{a/oxl}}{Z})$$

$$(mAl+nTi+oCb+pTa)_{25-\Sigma Al_S} + \frac{Fe_{a/oxl}}{Z} + \frac{Cr_{a/oxj}}{Z} + \frac{Mo_{a/oxk}}{Z} + \frac{W_{a/oxl}}{Z}$$
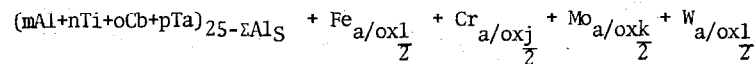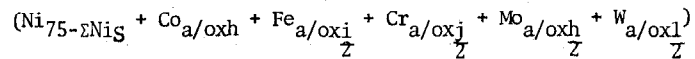
Where

ΣNi_S = Sum of carbide and boride-adjusted atomic percentages
of the nickel-substituting elements in the gamma-prime.

ΣAl_S = Sum of carbide and boride adjusted atomic percentages
of the aluminum-substituting elements in the gamma-prime.

and a/o = Atomic percentage of the relevant element after the
removal of carbides and borides from the matrices.

Nv Calculation

No changes are made here. The sum of the product of the residual atom
percentages and their appropriate multipliers, gives the final Nv number.

Constants

Constant	Assigned Value	
a	3.5 a/o	upper limiting value of Mo + W in M_6C calculation
b	0.4 a/o	upper limiting value of Cb + Ta in MC calculation
c	0.5	proportion of C entering MC
d	Mo_6C	composition of M_6C
e	$(Cb_{0.6}Ti_{0.2}Mo_{0.2})C$	composition of MC in presence of Cb or T
f	$(Ti_{0.8}Mo_{0.2})C$	composition of MC in absence of Cb
g	$(Cr_{0.9}Mo_{0.1})_{23}C_6$	composition of $M_{23}C_6$
h	0.23	maximum solubility of Co in gamma-prime
i	0.15	maximum solubility of Fe in gamma-prime
j	0.16	maximum solubility of Cr in gamma-prime
k	0.01	maximum solubility of Mo in gamma-prime
l	0.01	maximum solubility of W in gamma-prime
m	1.0	proportion of Al entering gamma-prime
n	1.0	proportion of Ti entering gamma-prime
o	1.0	proportion of Cb entering gamma-prime
p	1.0	proportion of Ta entering gamma-prime
q	5.66	electron vacancy multiplier for V
r	4.66	electron vacancy multiplier for Mo
s	4.66	electron vacancy multiplier for W
t	4.66	electron vacancy multiplier for Cr
u	4.66	electron vacancy multiplier for Zr
v	3.66	electron vacancy multiplier for Mn
w	2.66	electron vacancy multiplier for Fe
x	1.71	electron vacancy multiplier for Co
y	0.61	electron vacancy multiplier for Ni
z	0.00	electron vacancy multiplier for Cu
a'	1.5	atomic proportion of Mo to B

Sample Calculation of Variable

Precipitation Prediction Program for 713C

	w/o	At Wt.	w/o/at Wt.	a/o	C' & B' adj.	γ' adj.	a/o
C	0.08	12.01	.0066	.36	–	–	–
Mo	4.42	95.95	.0462	2.54	2.393	2.369	6.30
W	–	183.92	–	–	–	–	–
Cb	2.66	92.91	.0286	1.57	1.354	–	–
Ta	–	180.88	–	–	–	–	–
Ti	0.81	47.90	.0169	0.93	0.858	–	–
Cr	13.68	52.01	.2630	14.45	14.45	13.294	35.30
Co	–	58.94	–	–	–	–	–
Fe	–	55.85	–	–	–	–	–
Al	6.20	26.97	.2300	12.65	12.65	–	–
B	.009	10.82	.0009	.05	.05	–	–
Zr	.06	91.22	.0006	.03	.03	.030	.08
V	–	50.95	–	–	–	–	–
Ni	72.08	58.69	1.2300	67.70	67.70	21.934	58.30
			1.8228	100.28	99.560	37.627	99.98

Carbide Calculation – read constants a, b, c, d, e, f and g
1) Mo + W is less than 3.5(a) so no M_6C is formed
2) Cb+Ta = 1.57 a/o, which is > 0.4(b) so all C goes to form
carbide of composition (e) $(Cb_{0.6}Ti_{0.2}Mo_{0.2})C$ and since C = .36% there
will be .36 x 0.6 Cb = .216 a/o Cb, .36 x 0.2 Ti = .072 a/o Ti and
.36 x .2 = .072% Mo to be removed from the matrix as carbide.

Boride Calculation – read constant a'
Multiply B a/o by 1.5 (a') = .05 x 1.5 = .075 B to be removed
as boride.

Gamma-Prime Calculation ($Ni_{75}Al_{25}$ as base) read constant h, i, j,
k, l, m, n, o and p.
Elements on Al side of γ'

Al	12.65 x m = 12.65 x 1 =	12.650	
Ti	0.858 x m = 0.858 x 1 =	0.858	
Cb	1.354 x o = 1.354 x 1 =	1.354	
Ta	o x p =	0.0	
Fe	o x i =	0.0	
Cr	14.45 x $\frac{7}{j}$ = 14.45 x .08 =	1.156	

Mo   2.468 x $\frac{k}{2}$ = 2.468 x .005 = 0.012

W   0 x $\frac{1}{2}$ = 0.0   0.0

16.030 atoms per hundred

Elements on Ni side of γ'

Co   p x h =   0 x 0.23   =   0.0

Fe   o x $\frac{i}{2}$ =   0 x 0.15   -   0.0

Cr   14.45 x $\frac{j}{2}$ = 14.45 x .08 =   1.156

Mo   2.468 x $\frac{k}{2}$ = 2.468 x .005 =   .012

W   o x $\frac{1}{2}$ = 0 x .005   = $\underline{0.0}$

  1.168

Carbide and Boride Adjustment

The remaining C is therefore .36 - .36 = 0 a/o   C

The remaining Cb is therefore 1.57 - 0.216 = 1.354 a/o Cb

The remaining Ti is therefore 0.93 - 0.072 = 0.858 a/o Ti

The remaining Mo is therefore 2.54-(0.072+0.075)=2.393 a/o Mo

Since the formula is Ni_3Al, 16.030 atoms on the Al side will carry 16.030
x 3 - 48.090 atoms on the Ni side. Now the non-Ni atoms on the Ni side =
1.168 (Cr+Mo) so the Ni atoms will be 48.090-1.168=46.922 atoms.
    So the γ' composition is (in atoms)

Ni	Cr	Mo	Al	Ti	Cb
46.922	2.312	.024	12.650	0.858	1.354

and these amounts must be subtracted in the γ' adjustment.

Gamma-Prime Adjustment

Subtract γ' composition (in atoms) from the "C' and B' adj." column and
enter in "γ' adjusted" column.

Calculate New Matrix a/o

By summing "γ' adj." column and ratioing to 100%.

Calculation of N_v Number

Read constants q, r, s, t, u, v, w, x, y, and z.

Mo   6.30   x   n   =   0.063   x   4.66   =   .294

Cr   35.30   x   p   =   0.353   x   4.66   =   1.643

Zr   .08   x   q   =   0.008   x   4.66   =   .037

Ni   58.98   x   u   =   0.5898 x   0.61   = $\underline{.359}$

  2.333

N.B.   Print out (1) original chemistry of alloy   (2) all constants
       used   (3) matrix composition a/o (after precipitation of carbides,
       borides and gamma prime) (4) gamma-prime composition.

Comparison

The gamma prime distribution is:

Ni	Cr	Mo	Al	Ti	Cb	Cr	Mo
46.922,	1.156,	0.012	12.650,	0.858,	1.354,	1.156,	.0012

The sum of these atoms is 64.120 and chemical formula is:

2.93	0.073	0.001	.747	.053	.084	.072	.001

or

$(0.98 \quad 0.02 \quad 0.003)_3$ 0.75   .05   .08   .07   .01

Decker and Bieber

$(0.95 \quad 0.03 \quad 0.02)_3$ 0.80   0.06   0.14

APPENDIX III

Calculation for Udimet 700

	w/o	At Wt.	w/o/At Wt.	a/o	C' adj.	B' adj.	γ' adj.	a/o
C	0.06	12.01	.0050	0.28	–	–	–	
Mo	4.45	95.95	.0464	2.56	2.479	2.269	2.247	5.25
Ti	3.45	47.90	.0720	3.98	3.868	3.878	–	
Cr	14.60	52.00	.2810	15.45	14.966	14.966	12.574	29.45
Co	17.60	58.94	.2970	16.45		16.450	12.660	29.65
Al	4.37	26.97	.1617	8.93		8.930	–	
B	.028	10.82	.0026	0.14		–		
Fe	0.14	55.85	.0025	0.14		0.140	0.110	0.26
	44.70							
Ni	55.30	58.69	.9420	52.20		52.200	15.152	35.05
			1.8110	100.13			42.743	99.66

Carbide

$$0.14 \text{ C} \rightarrow (\text{Ti}_{0.8}\text{Mo}_{0.2})\text{C} \quad \begin{array}{l} \text{Ti} = 0.8 \times 0.14 = .112 \\ \text{Mo} = 0.2 \times 0.14 = .028 \end{array}$$

$$0.14 \text{ C} \rightarrow (\text{Cr}_{0.9}\text{Mo}_{0.1})_{23}\text{C6} \quad \text{Cr} = 3.45 \times 0.14 = .484$$
$$\text{or} \quad (\text{Cr}_{3.45}\text{Mo}_{0.38})\text{C} \quad \begin{array}{l} \text{Mo} = 0.38 \times 0.14 = .053 \\ \Sigma \text{ Mo} \qquad\qquad\qquad .081 \end{array}$$

Boride

$$0.14 \text{ B} \rightarrow \text{Mo}_3\text{B}_2 \qquad \text{Mo} = 1.5 \times 0.14 \qquad .21$$

Gamma-Prime

Elements on Al side

Al	8.930	x	1	=	8.930	
Ti	3.868	x	1	=	3.868	
Fe	0.14	x	$\frac{.15}{2}$	=	0.015	
Cr	14.966	x	$\frac{.16}{2}$	=	1.196	
Mo	2.269	x	$\frac{.01}{2}$	=	0.011	
					14.020	

79

Elements on Ni side

Co	16.45	x	0.23	=	3.790
Fe	0.14	x	$\frac{0.15}{2}$	=	0.015
Cr	14.966	x	$\frac{0.16}{2}$	=	1.196
Mo	2.269	x	$\frac{0.01}{2}$	=	$\frac{0.011}{5.012}$

14.020 Al-side atoms carry 14.020 x 3 Ni-side atoms

$$= 42.060$$

but $\underline{\quad 5.012\quad}$ are Ni substitutes

so $\quad 37.048$ are Ni atoms

N_v Calculation

Mo	.0525	x	4.66	=	0.244
Cr	.2945	x	4.66	=	1.371
Fe	.0026	x	2.66	=	.007
Co	.2965	x	1.71	=	.496
Ni	.3505	x	0.61	=	$\underline{\quad .214\quad}$
					2.332

Gamma-Prime Prediction

Ni	Co	Fe	Cr	Mo	Al	Ti	Fe	Cr	Mo
37.05	3.79	0.01	1.20	0.01	8.93	3.87	0.01	1.20	0.01

Sum of atoms = 42.060 + 14.020 = 56.08 atoms

| 2.64 | 0.27 | neg. | 0.09 | neg. | 0.64 | 0.28 | neg. | 0.09 | neg. |

and the chemical formula would be

$$(Ni_{0.88}Co_{0.09}Cr_{0.03})_3 \ (Al_{0.64}Ti_{0.28}Cr_{0.09})$$