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ESTIMATION OF GAMMA PHASE COMPOSITION IN NICKEL-BASE SUPERALLOYS (BASED ON GEOMETRIC ANALYSIS OF A FOUR-COMPONENT PHASE DIAGRAM)

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16. Abstract

The gamma-gamma prime region of the nickel-aluminum-chromium-titanium system at 750° C has been analyzed through the use of phase rule principles and analytic geometry to allow estimation of gamma phase composition when the composition of a two-phase quaternary alloy is known. By application of currently used phase computation methods with the above calculation, the gamma phase composition of several nickel-base superalloys was estimated and found (except for tungsten) to be in good agreement with compositions for these alloys as reported in the literature.

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SUMMARY

The nickel-rich region of the nickel-aluminum-chromium-titanium system is the basis for describing the gamma-gamma prime phase relationships in most nickel-base superalloys. The gamma-gamma prime region of this system at 750° C has been analyzed by first making a few simplifying assumptions about the shape of solvus surfaces and the behavior of tie lines. By applying phase rule principles and analytical geometry to the simplified system, a closed form solution is obtained which allows the estimation of the gamma composition given the composition of a two-phase quaternary alloy.

By application of currently used phase computation methods with the above calculation, the gamma phase composition of several nickel-base alloys was estimated and found (except for tungsten) to be in good agreement with compositions of gamma phase reported in the literature.

Average electron vacancy concentrations $\left(\overline{N}_v\right)$ were calculated for the matrix compositions estimated by the above method for alloys whose stability relative to sigma or mu phase formation had been reported in the literature. It was not possible to set a single critical $\overline{N}_v$ below which no alloys formed mu or sigma phase and above which all alloys formed these phases.

INTRODUCTION

The nickel-base superalloys used in gas turbines are placed in service in a metastable condition. A decade ago when gas turbines were designed for hundreds of hours instead of the thousands of hours required today, the lack of metallurgical stability of these alloys was of little consequence. In the past several years, however, several investigators have observed that a few of the commercial nickel-base superalloys will precipitate sigma phase and other related intermetallic compounds when subjected to prolonged exposures at elevated temperatures. In some alloys, loss of stress rupture life and a decrease in low temperature ductility have been correlated with the precipitation of the intermetallic compounds.

In an effort to predict this type of instability and to be able to adjust composition during melting to avoid unstable compositions in these alloys, several schemes have been proposed which relate the chemistry of the gamma (face-centered-cubic matrix) phase in these alloys to melt chemistry (refs. 1 and 2). After estimating the chemical composition of the gamma phase, the average electron vacancy concentration $\left(\overline{N}_v\right)$ may be calculated for the gamma phase. The $\overline{N}_v$ is then compared to an empirically selected critical $\overline{N}_v$ to determine the propensity of the alloy toward the formation of intermetallic compounds. Alternatively the estimated gamma phase chemistry may be compared to published phase diagrams to determine the stability of the alloy.

It is beyond the scope of this report to deal with all the ramifications of this type of calculation; however, it is the objective of this work to show how published phase diagrams can be used to predict the gamma chemistry using well-founded phase-rule principles and analytic geometry. In a previous publication (ref. 3), I suggested an analysis based on the nickel-chromium-aluminum system.

In this report, one approach will be demonstrated for simplifying a two-phase region of a quaternary phase diagram so that it can be easily analyzed geometrically. Specifically, a method is developed to allow the estimation of the composition of the gamma phase given the composition of a two-phase (gamma plus gamma prime) alloy in the nickel-aluminum-chromium-titanium system. This estimation method is then applied to nickel-base superalloys and the results of the estimation method are compared to published gamma phase chemical analyses. Finally, the electron vacancy approach to predicting alloy stability using this gamma composition estimation method is discussed.

ANALYSIS OF PHASE DIAGRAMS

Definitions

The construction, analysis, and interpretation of phase diagrams are described in several well-known texts (refs. 4 to 6). However, listed here are a few definitions and general properties of phase diagrams and the nomenclature used in describing multicomponent phase diagrams which are used in the analysis to be described.

The solvus surface is the surface which represents the limit of solid solubility of the components in a solid phase. This report will deal only with isothermal sections.

Therefore, in a ternary diagram the solvus will be a line and in a quaternary diagram it will be a three-dimensional surface.

Tie lines (conodes) are straight lines which connect those compositions (of two phases in a two-phase field) which are in equilibrium. They are isothermal lines, and Gibbs' phase rule requires that they not intersect in the two-phase field. Furthermore, the boundary between a two-phase field and a three-phase field in an isothermal section of a ternary diagram is a tie line. This is shown in figure 1 as line A-B. In a two-phase field of a binary diagram any isothermal line between two solvus lines is a tie line. Therefore, in a ternary diagram, the limit of a two-phase field on a binary edge of the diagram is also a tie line. This is shown in figure 1 as line C-D.

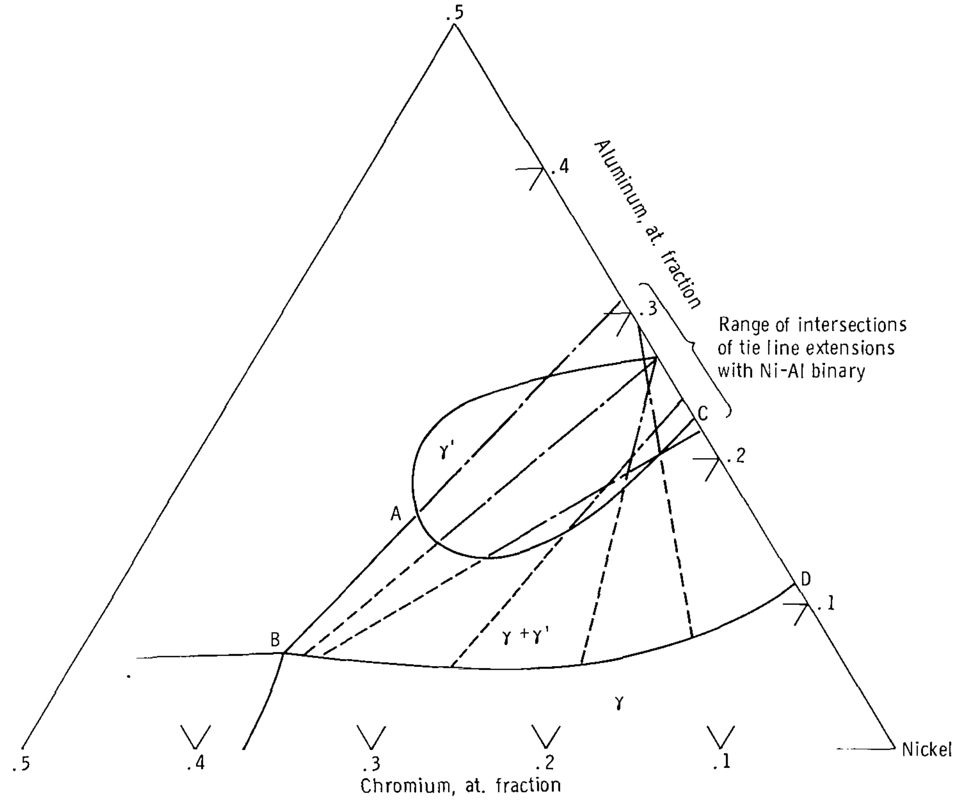


Figure 1. - Nickel-rich region of Ni-Cr-Al system at 750° C (After Taylor and Floyd (ref. 7)).

This last point is noted because most ternary metallurgical phase diagrams available in the literature do not show tie lines; however, the two tie lines mentioned are always available in isothermal sections. The availability of these tie lines may assists in applying the technique which is described to other systems.

In this report the following notation will be used to refer to solvus surfaces. The gamma-gamma prime solvus is the boundary representing maximum solubility of elements in gamma. The adjacent phase field to the gamma field is gamma plus gamma prime. A gamma prime-gamma solvus would then describe the boundary between the gamma prime field and the two-phase gamma plus gamma prime field.

Approach

A general statement of the problem is that the gamma chemistry of an alloy in the two-phase field is to be determined given the composition of the two-phase alloy. This can be restated as finding the intersection of the tie line on which the two-phase alloy lies and the gamma-gamma prime solvus surface. A solution to this is available through the use of analytic geometry. Specifically, finding the intersection of a line and a surface is desired. As a first step, curve fitting allows us to express the solvus as an equation. The problem is now reduced to finding an expression for the tie line on which the two-phase alloy lies. In an earlier report (ref. 3), I described this solution for the nickel-chromium-aluminum ternary system.

A solution for the quaternary system nickel-aluminum-chromium-titanium will now be developed. This report demonstrates how one can apply analytic geometry to phase diagrams to obtain a solution, but is not intended to offer a specific type of solution. To assist in following the analysis of the quaternary system, the nickel-rich regions of the ternary systems which bound the region of interest in the quaternary system will be described briefly.

Ternary Diagrams

The ternary phase diagrams relevant to the nickel-rich region of the nickel-aluminum-chromium-titanium system are shown in figures 1 to 3 and were taken from references 7, 8, and 9. Note that fortunately the investigators did determine tie lines in these systems. As discussed in reference 3, the gamma-gamma prime solvus curve in the nickel-aluminum-chromium system may be approximated by

$$\mathrm{Al} = 1.33\ \mathrm{Cr}^2 - 0.566\ \mathrm{Cr} + 0.12 \tag{1}$$

where

Al = atomic fraction aluminum in gamma

Cr = atomic fraction chromium in gamma

Further, if the tie lines in figure 1 are extended to the nickel-aluminum binary edge of the diagram, they intersect it between 0.23 and 0.32 aluminum. To obtain a solution in reference 3, I forced all tie lines to intersect at 0.27 aluminum. This simplification (that the tie lines did intersect) allowed a closed form solution, with the tie line equation being defined by the point of tie line intersection and the composition of the alloy in the two-phase field. To further simplify the geometry, in this report I shall force the tie lines to intersect at 0.25 aluminum instead of 0.27.

Let us now examine the nickel-chromium-titanium ternary diagram (fig. 2). It can be seen that the gamma-eta tie lines intersect at 0.25 titanium because there is no reported solubility of nickel or chromium in eta. A comparison of the gamma-gamma prime solvus in the nickel-aluminum-chromium system to the gamma-eta solvus in the nickel-titanium-chromium system shows that titanium and aluminum behave similarly in the nickel-rich region of the nickel-chromium- (aluminum or titanium) system. Titanium, however, is slightly less soluble in the gamma phase than is aluminum.

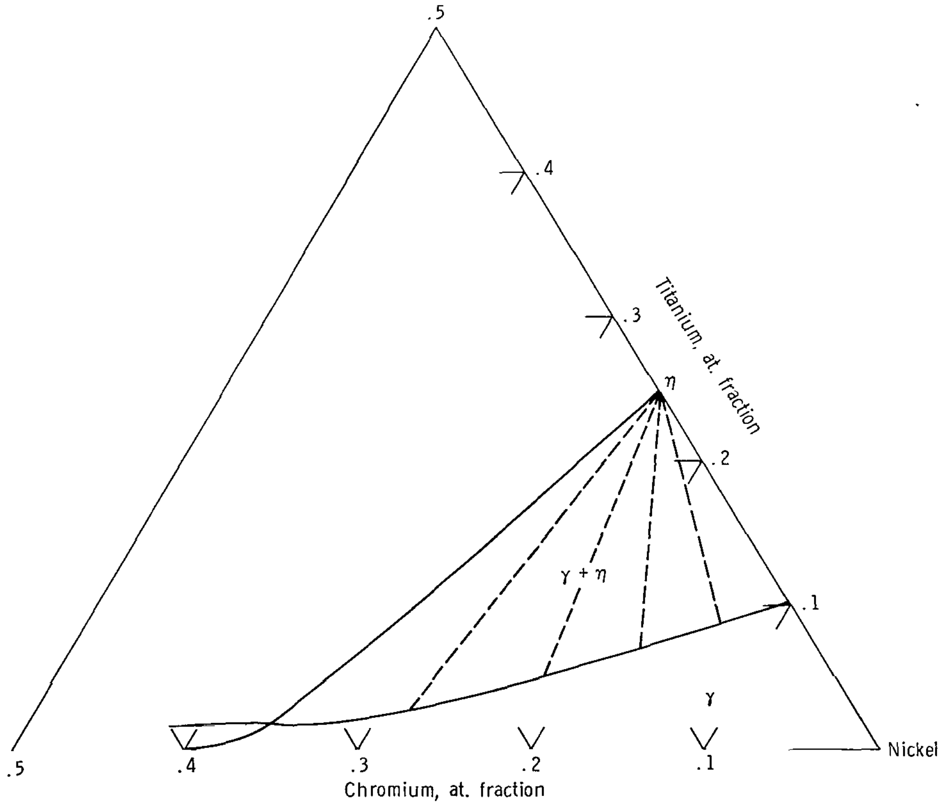


Figure 2. - Nickel-rich region of Ni-Cr-Ti system at 750° C (after Taylor and Floyd (ref. 8)).

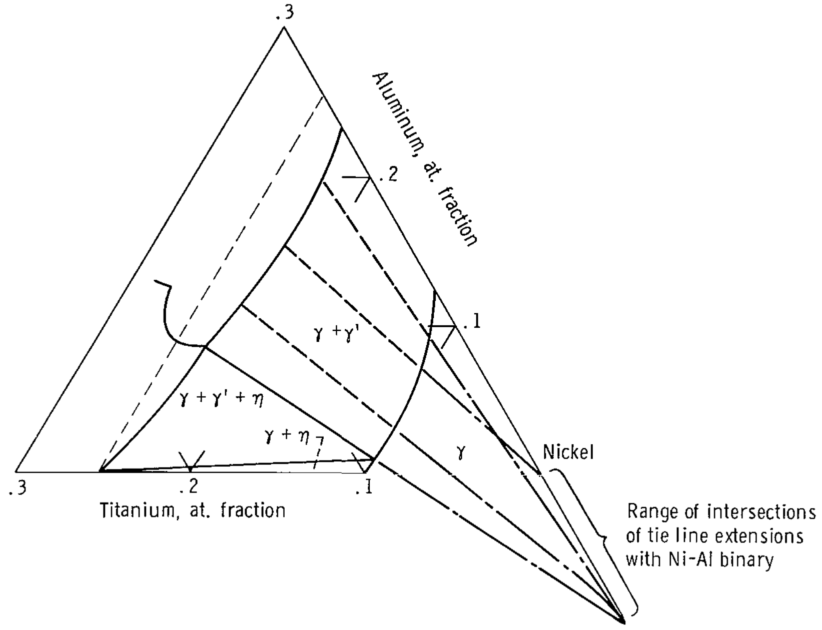


Figure 3. - Nickel-rich region of Ni-Ti-Al system at 750° C (after Taylor and Floyd (ref. 9)).

The third ternary diagram which is required (nickel-titanium-aluminum) is shown in figure 3. To simplify this diagram I have assumed the gamma-gamma prime solvus to be the linear equation

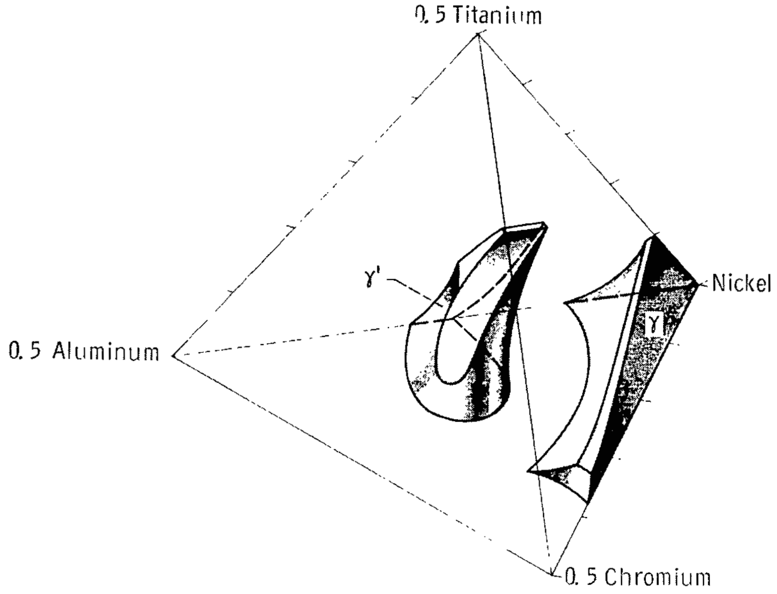
$$\mathrm{Al} = -1.5\ \mathrm{Ti} + 0.12 \tag{2}$$

This appears to be adequate for our purpose below 0.05 titanium. Further, if the tie lines shown are extended to the nickel-aluminum binary edge, they will intersect outside of the ternary diagram on an extension of the binary between 0.0 and -0.1 aluminum. For this report I will assume a common-point of tie line intersection at -0.05 aluminum.

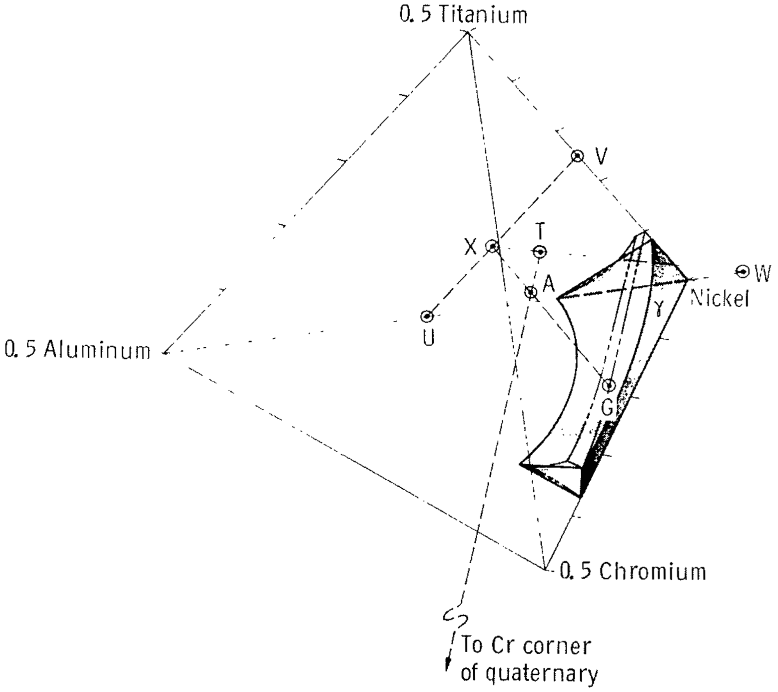
Quaternary Diagram

The quaternary diagram, nickel-aluminum-chromium-titanium is shown in figure 4(a). Only the gamma and gamma prime fields are shown in this figure. The details are available in reference 10. I have approximated the gamma-gamma prime solvus with the following equation which is obtained directly from equations (1) and (2):

$$\mathrm{Al} + 1.5\ \mathrm{Ti} = 1.33\ \mathrm{Cr}^2 - 0.566\ \mathrm{Cr} + 0.12 \tag{3}$$



(a) Diagram after Taylor (ref. 10).



(b) Geometric construction of solution for gamma phase composition.

Figure 4. - Nickel-rich region of Ni-Al-Cr-Ti system at 750° C.

This surface is shown shaded in figure 4(b), while the true solvus can be seen "ghosted" (double dot-dashed curves) in the same figure. The approximation appears to be adequate at low titanium levels.

The next step is to deduce the tie line behavior in the alloy system. In the three ternary systems, points of tie line intersection can be reasonably assumed. These points occur at (nickel, 0.25 aluminum), (nickel, -0.05 aluminum) and (nickel, 0.25 titanium). It should be apparent that the concept of a single point of intersection such as that used in reference 3 would not be adequate to describe the tie line behavior in the quaternary system.

Any description of the tie lines must include the above intersections as limiting cases and the tie lines must not intersect in a two-phase field. A further condition which should be met is described in reference 10 where Taylor indicates that, in a section through the quaternary with nickel constant at 0.75, the tie lines lie almost in the plane of the section. Such a model will now be developed.

At low titanium concentrations the tie line description that will now be presented is consistent with these boundary conditions; however, it is not the only solution possible. It will, as will be demonstrated, allow a closed form solution to the geometric problem which is in reasonable agreement with published data.

In the limiting ternary diagrams (figs. 1 to 3), it has been shown that the tie lines can be simplified by assuming they have common points of intersection. The assumed intersection is at 0.25 aluminum and 0.75 nickel in the nickel-aluminum-chromium system, and at 0.25 titanium and 0.75 nickel in the nickel-titanium-chromium system. It is reasonable to assume that in the quaternary system all tie lines will emanate from a line connecting these two points (U and V, fig. 4(b)).

The assumption that the tie lines in the nickel-aluminum-titanium system intersect at -0.05 aluminum is used to establish, as a function of the aluminum to titanium ratio of the two-phase quaternary alloys, the point on U-V from which the tie lines emanate. This point moves systematically from U when the titanium is zero toward V as the titanium increases.

In the specific construction to be used, a tie line is formed by the intersection of two planes. One plane has a zone axis (for this report defined as a line common to all planes in the set) Cr-W (fig. 4(b)). The other plane has U-V as a zone axis. The aluminum to titanium to nickel ratio of the alloy governs the selection of the plane from the Cr-W set and the chromium concentration selects the plane from the U-V set.

Because U-V and Cr-W are zone axes for the two planes determining the tie line, the only places where the tie line families can intersect are on U-V or Cr-W. Both of these lines are outside of the two-phase field; therefore, Gibbs' phase rule is followed.

The details of the construction by which the composition of the gamma phase in a two-phase quaternary alloy is determined from the above analysis follows. In figure 4(b) the composition of the two-phase quaternary alloy is projected on the nickel-aluminum-titanium diagram by passing a line from the chromium corner of the quaternary, through the two-phase alloy A to the nickel-aluminum-titanium ternary. This construction locates a point T in the ternary diagram that has the same relative nickel, aluminum, and titanium concentration as in the quaternary alloy. This is shown as line Cr-A-T. The intersection of U-V (the line connecting 0.25 aluminum, 0.75 nickel and 0.25 titanium, 0.75 nickel) and T-W (the tie line in the nickel-aluminum-titanium ternary) establishes point X on the tie line (containing the two-phase quaternary alloy A). The tie line on which alloy A lies is X-A-G. The composition of G (gamma phase) is determined by finding the intersection of X-A with the solvus surface.

The mathematical solution follows.

The coordinates of T may be expressed as

$$Al_T = \frac{Al_A}{Al_A + Ti_A + Ni_A} \tag{4}$$

$$Ti_T = \frac{Ti_A}{Al_A + Ti_A + Ni_A} \tag{5}$$

This follows from the geometric construction of the line Cr-A-T which results in the relation

$$\frac{Al_T}{Al_T + Ti_T + Ni_T} = \frac{Al_A}{Al_A + Ti_A + Ni_A}$$

where

$$Al_T + Ti_T + Ni_T = 1$$

and

Ni = nickel concentration

Al = aluminum concentration

Ti = titanium concentration

subscript T at point T

subscript A in two-phase alloy

The coordinates of X are found in the following way. U-V is

$$\mathrm{Al} + \mathrm{Ti} = 0.25 \tag{6}$$

and the tie line in the nickel-titanium-aluminum ternary is

$$\mathrm{Al} + 0.05 = m\ \mathrm{Ti}$$

Therefore,

$$m = \frac{\mathrm{Al}_T + 0.05}{\mathrm{Ti}_T} \tag{7}$$

where m is the slope of the line through T. Solving equations (6) and (7) simultaneously defines titanium at point X,

$$\mathrm{Ti}_X = \frac{0.3}{\dfrac{\mathrm{Al}_T + 0.05}{\mathrm{Ti}_T} + 1} \tag{8}$$

and substituting Ti_X in equation (6) defines aluminum at point X

$$\mathrm{Al}_X = 0.25 - \mathrm{Ti}_X \tag{9}$$

The coordinates of X and A define the tie line which may be expressed in two-point form as

$$\frac{\mathrm{Ti}_A - \mathrm{Ti}_X}{a} = \frac{\mathrm{Al}_A - \mathrm{Al}_X}{b} = \frac{\mathrm{Cr}_A - \mathrm{Cr}_X}{c} \tag{10}$$

where $c = 1$ and $\mathrm{Cr}_X = 0$. Equation (10) is solved for the direction numbers a and b; then, equation (10), written in general form for lines through point X, and equation (3) are solved simultaneously to yield the coordinates of point G,

$$\mathrm{Cr}_G = \frac{-B + \sqrt{B^2 - 4AC}}{2A} \tag{11}$$

$$\mathrm{Al}_G = \mathrm{Cr}_G b + \mathrm{Al}_X \tag{12}$$

$$\mathrm{Ti}_G = \mathrm{Cr}_G a + \mathrm{Ti}_X \tag{13}$$

where

$A = 1.33$

$B = -(0.566 + 1.5a + b)$

$C = 0.12 - Al_X - 1.5Ti_X$

The composition of the gamma phase is shown in equations (11), (12), and (13). The balance of course is nickel.

APPLICATIONS TO NICKEL-BASE SUPERALLOYS

Calculation of Gamma Phase Composition

Commercial nickel-base superalloys contain up to 12 alloy elements. Those elements commonly added to nickel (Ni) are cobalt (Co), iron (Fe), carbon (C), chromium (Cr), molybdenum (Mo), tungsten (W), aluminum (Al), titanium (Ti), zirconium (Zr), niobium (Nb), tantalum (Ta), and vanadium (V). In addition small quantities of silicon (Si), manganese (Mn), and boron (B) may also be present. All of these are not necessarily in a single alloy.

To calculate the composition of the gamma phase in a nickel-base superalloy by the proposed method, it must be reduced to the Ni-Al-Cr-Ti quaternary system. First, a calculation similar to that proposed by Woodyatt, Sims, and Beattie (ref. 2) is used to eliminate carbon and boron from the system.

Specifically, it is assumed that all boron forms an M_3B_2 boride having the composition $(Mo_{0.5}, Ti_{0.15}, Cr_{0.25}, Ni_{0.1})_3 B_2$. It is then assumed that 75 percent of the carbon in the alloy forms monocarbides (MC) in the sequence TiC, TaC, NbC, ZrC, and VC (i.e., TiC forms first). This sequence of monocarbide formation and the distribution of carbon between monocarbides and complex carbides are used in contrast to those proposed in reference 2 to force the Ti to the lowest possible level. Further, the monocarbides are assumed in this report to be nonstoichiometric in that it is assumed that the formula is given as

$$MC = \left\{ M^*_{[1-0.04(Mo_a+W_a)]}(Mo + W)_{0.04(Mo_a+W_a)} \right\} C$$

where M^* is Ta, Nb, and so forth and where $(Mo_a + W_a)$ are atomic percent in the melt. That is, the Mo and W concentrations in the M fraction of MC are four times the Mo and W concentrations of the original melt. The above composition for the monocarbides was developed from a combination of compositions which have been reported in the literature and from unpublished data obtained in this laboratory. The remaining 25 percent of the carbon is assumed to form complex carbides ($M_{23}C_6$ or M_6C). The $M_{23}C_6$ is assumed to have the composition $(Cr_{21}Mo_2)C_6$ and the M_6C to have the composition $\left[Ni_{2.5}Co_1Cr_{0.5}(Mo + W)_2\right]C$. The selection of $M_{23}C_6$ or M_6C is based on the correlation proposed earlier by the author (ref. 11). Specifically, $M_{23}C_6$ forms if

$$Cr > 3.5(Mo + 0.4\ W)$$

Otherwise, M_6C will form.

The carbon and boron have now been accounted for. However, to further reduce the alloy to one containing only Ni, Al, Cr, Mo, W, Co, and Fe, an additional assumption must be made concerning the Nb, Ta, Zr, and V not accounted for by carbide formation. All the Nb, Ta, Zr, and one-half of V remaining are assumed to enter the gamma prime phase. This gamma prime will then be

$$(Ni, Co, Fe)_{3.3}(Nb, Ta, Zr, 1/2\ V)$$

The form $Ni_{3.3}X$ is used in place of the more common Ni_3X, because the gamma prime-gamma solvus in the Nb-Ni and Ta-Ni diagrams at 750° C is approximately 23 percent (ref. 12). It is recognized that the use of the above formula to express a composition for gamma prime together with the geometric analysis implies the formation of two gamma primes. However, the use of the $Ni_{3.3}X$ gamma prime is strictly an artificial mathematical construction and is the final step in reducing the alloy to the Ni-Cr-Ti-Al-Mo-W-Fe-Co system. It is consistent with the approach used in current methods for handling these elements.

In reference 3, I assumed that Mo and W can be treated as being in two ternary systems which are independent of each other and the Ni-Cr-Al system with linear gamma-gamma prime solvus curves. The same philosophy is used herein except that they are now considered as independent quaternary systems (W or Mo)-Ni-Al-Ti. Tie lines are assumed to intersect at Ni, 0.25 Al. The gamma-gamma prime solvus is planar passing through 0.12 Al, 0.88 Ni; 0.10 Ti, 0.9 Ni; and 0.15 Mo or W, 0.85 Ni. The concentration of Mo and/or W in gamma is

$$Mo_G \text{ or } W_G = \frac{0.15[(0.13(Mo_A \text{ or } W_A)]}{0.15(0.25 - Al_A - 1.2Ti_A) - 0.12(Mo_A \text{ or } W_A)} \tag{14}$$

The only elements now left in excess of the quaternary diagram are Co and Fe. During the phase diagram calculation, these are treated as if they are Ni and are separated in proportion to their concentration in the melt after it is depleted of borides and carbides.

To summarize, the gamma chemistry is estimated by the following steps:

(1) Convert weight percent to atomic percent.

(2) Adjust for boride formation.

(3) Adjust for monocarbide formation.

(4) Adjust for complex carbide formation.

(5) Adjust for pseudo gamma prime $(Ni, Co, Fe)_{3.3}(Nb, Ta, Zr, 1/2\ V)$.

(6) Reconvert the remaining elements to atomic fraction to obtain Al_A, Ti_A, and so forth.

(7) Apply equation (14).

(8) Apply equations (4), (5), (8), (9), (10), and (11) to determine Cr in gamma.

(9) Substitute $Cr_A + Mo_A + W_A$ for Cr_A in equation (10); then apply equations (10), (11), (12), and (13) to determine Al and Ti.

(10) Determine Ni + Fe + Co by

$$Ni_G + Co_G + Fe_G = 1 - Cr_G - Mo_G - W_G - Al_G - Ti_G$$

(11) Separate Ni_G, Co_G, and Fe_G according to the amount present in the melt after adjusting for borides and carbides

$$Ni_G = \frac{(Ni_G + Co_G + Fe_G)(Ni_A)}{Ni_A + Co_A + Fe_A}$$

and so forth.

(12) Make empirical adjustment for Ti and Co bias if desired. (See next section for details.)

Comparison of Calculated and Analyzed Chemistries

This calculation sequence summarized above was programmed in FORTRAN IV and applied to the alloys reported by Kriege and Baris (ref. 13). The computed gamma compositions were generally found to be in good agreement with those determined by the chemical analysis of Kriege and Baris except that the Co estimate was low and the Ti estimate was high. To enhance the engineering utility of the method, an empirical correction was made to force the average value for Co and Ti to agree with the data of reference 13. The Co was adjusted by adding 5.6 percent to the Co (if present) and subtracting the same quantity from Ni. The Ti was adjusted by multiplying the Ti by 0.36, the difference (0.64 Ti) being added to Ni.

TABLE I. - COMPOSITION OF GAMMA IN SELECTED SUPERALLOYS

(a) Comparison with data of Kriege and Baris (ref. 13)

Alloy	Weight percent (balance is nickel)															
	Chromium		Aluminum		Titanium		Cobalt		Iron		Molybdenum		Tungsten		Vanadium	
	Reference 13	Present work	Reference 13	Present work	Reference 13	Present work	Reference 13	Present work	Reference 13	Present work	Reference 13	Present work	Reference 13	Present work	Reference 13	Present work
B-1900	16.4	14.9	2.4	2.5	---	0.1	16.4	15.1	----	---	9.0	9.4	----	----	---	---
GMR 235	18.8	19.1	1.8	2.0	0.5	.4	----	----	12.1	9.7	5.4	4.7	----	----	---	---
Inconel 700	17.7	17.0	1.9	1.6	.8	.5	33.3	34.3	.7	.7	4.0	3.5	----	----	---	---
Alloy 713C	22.6	24.0	3.9	3.2	.1	.1	----	----	----	---	6.6	8.1	----	----	---	---
Inconel X-750	16.3	14.5	.3	1.0	1.0	.9	----	----	7.5	6.5	----	---	----	----	---	---
IN 100	22.0	24.4	2.3	1.6	.4	.8	24.0	18.4	----	---	5.3	8.0	----	----	---	0.4
Mar-M 200	17.3	12.4	1.4	1.8	---	.3	12.9	14.3	----	---	----	---	12.0	16.9	---	---
Nicrotung	22.5	19.0	.4	1.3	.8	.7	14.9	14.3	----	---	----	---	8.8	12.4	---	---
Nimonic 115	24.4	24.8	2.2	1.8	.5	.6	20.5	19.3	----	---	4.9	4.9	----	----	---	---
René 41	23.6	20.9	.6	1.1	.6	.9	12.8	16.2	----	---	11.4	9.6	----	----	---	---
TRW 1900	21.5	19.5	3.5	2.6	.3	.1	15.5	14.1	----	---	----	---	9.4	16.8	---	---
Udimet 500	26.0	23.3	1.1	1.5	.5	.7	25.9	24.5	----	---	5.0	4.2	----	----	---	---
Udimet 700	22.3	23.9	2.5	1.8	1.3	.6	24.4	22.9	----	---	6.6	6.8	----	----	---	---
Uditemt AF 1753	19.6	18.8	1.1	1.1	.9	.7	8.8	13.4	11.2	9.1	1.7	1.2	8.3	7.3	---	---
Waspaloy	22.5	20.0	.5	.9	.6	.8	16.4	18.8	----	---	5.3	3.3	----	----	---	---

(b) Comparison with data computed from Mihalisin and Pasquine (ref. 14)

Alloy	Weight percent (balance is nickel)															
	Chromium		Aluminum		Titanium		Cobalt		Iron		Molybdenum		Tungsten		Vanadium	
	Reference 14	Present work	Reference 14	Present work	Reference 14	Present work	Reference 14	Present work	Reference 14	Present work	Reference 14	Present work	Reference 14	Present work	Reference 14	Present work
Alloy 713LC (heat 07)	18.7	21.0	3.6	2.8	0.4	0.1	----	----	----	0.2	6.0	6.3	----	----	---	---
Alloy 713LC (heat 17)	21.0	21.3	3.1	2.8	.2	.1	----	----	----	.1	6.6	6.2	----	----	---	---
Alloy 713C	21.4	22.0	2.9	2.9	.3	.1	----	----	----	.1	6.5	6.2	----	----	---	---
IN 731 X	18.1	21.0	1.8	1.5	---	.6	15.8	14.7	----	.2	3.5	4.4	----	----	1.4	0.4

TABLE II. - COMPOSITION OF ALLOYS

Alloy	Reference	Heat treatment	Weight percent (balance is nickel)											
			Cr	Co	Al	Ti	W	Mo	Nb	Ta	V	Fe	C	B
B-1900	13	1	7.9	9.8	5.9	1.0	----	5.7	-----	4.5	----	----	0.09	----
GMR 235		1	15.9	-----	3.5	2.0	----	5.0	-----	---	----	9.8	.15	----
Inconel 700		2	14.3	28.5	3.0	2.5	----	3.9	-----	---	----	.7	.12	----
Alloy 713C		1	12.6	-----	6.8	.8	----	4.7	2.1	---	----	----	.16	----
Inconel X-750		3	14.6	-----	.8	2.4	----	----	.8	---	----	6.5	.04	----
IN 100		1	9.8	15.0	5.6	5.7	----	3.1	-----	---	0.9	----	.19	----
Mar-M 200		1	8.9	9.5	4.5	1.9	12.3	----	1.1	---	----	----	.16	----
Nicrotung		1	11.0	9.9	4.4	4.2	8.0	----	-----	---	----	----	.07	----
Nimonic 115		4	14.8	14.8	4.8	3.9	----	3.5	-----	---	----	----	.14	----
René 41		5	19.0	10.7	1.5	3.1	----	9.7	-----	---	----	----	.09	----
TRW 1900		1	10.1	10.3	6.7	1.0	9.2	----	1.6	---	----	----	.14	----
Udimet 500		6	18.7	19.3	2.9	3.0	----	4.3	-----	---	----	----	.07	----
Udimet 700		7	15.4	18.8	4.4	3.4	----	5.0	-----	---	----	----	.06	----
Unitemp AF 1753		8	16.4	7.7	2.0	3.4	8.3	1.5	-----	---	----	9.0	.23	----
Waspaloy		9	18.6	13.0	1.4	2.9	----	4.2	-----	---	----	----	.05	----
Alloy 713C	14	1	13.23	-----	5.86	.79	----	4.46	[a]2.09	---	----	.10	.11	0.01
Alloy 713LC (heat 07)		1	12.32	-----	5.90	.72	----	4.46	[a]2.13	---	----	.20	.06	.01
Alloy 713LC (heat 17)		1	12.52	-----	5.90	.60	----	4.41	[a]2.10	---	----	.15	.03	.01
IN 731 X		1	9.60	9.72	5.60	4.66	----	2.46	-----	---	.85	.23	.16	.01

Heat treatment	Description
1	As cast
2	2160° F/ 2 hr/air cool + 1600° F/ 4 hr/air cool
3	2100° F/ 2 hr/air cool + 1550° F/ 24 hr/air cool + 1300° F/20 hr/air cool
4	2175° F/$1\frac{1}{2}$ hr/air cool + 2010° F/ 6 hr/air cool
5	1950° F/ 4 hr/air cool + 1400° F/ 16 hr/air cool
6	1975° F/ 4 hr/air cool + 1550° F/ 24 hr/air cool + 1400° F/16 hr/air cool
7	2140° F/ 4 hr/air cool + 1800° F/136 hr/air cool
8	2150° F/ 4 hr/air cool + 1650° F/ 6 hr/air cool
9	1975° F/ 4 hr/air cool + 1550° F/ 24 hr/air cool + 1400° F/16 hr/air cool

[a] Reported in ref. 14 as Nb + Ta.

TABLE III. - COMPARISON OF PROPOSED METHOD AND ANALYZED DATA

Element	Average difference, $\bar{d}$,[a] wt %	Sample standard deviation of difference, s_d
Cr	1.1	2.05
Al	.007	.57
Ti[b]	.007	.28
Co[b]	.017	2.74
Mo	.136	1.36
Fe	1.38	1.10
W	-3.73	3.52

[a] $\bar{d} = \sum_{i=1}^{n} \frac{\text{literature - calculated}}{n}$.

[b] $\bar{d}$ was forced to be essentially zero.

A comparison of the results of this adjusted computation and data from reference 13 and data of Mahalisin and Pasquine (ref. 14) is shown in tables I(a) and I(b), respectively. The reported melt chemistry and heat treatments for the alloys considered are shown in table II. The mean and standard deviation of the difference between the data of Kriege and Baris and the computed values are shown in table III.

It can be seen that on the average, except for W, the computed concentration of the elements in the gamma phase are in good agreement with those determined experimentally. Although the standard deviations appear to be large when compared to the average concentration for most of the elements, they do not appear excessive in the light of the assumptions currently required to permit a solution.

Application of Calculation of Gamma Chemistry to $\bar{N}_v$

An attempt was made to determine if the average electron vacancy concentration $\left(\bar{N}_v\right)$ of the matrix having a composition which was calculated by the method described could be used to predict alloy stability. Calculations of this type were conducted using the melt

TABLE IV. - AVERAGE ELECTRON VACANCY CONCENTRATION OF SELECTED ALLOYS

Alloy	Average electron vacancy concentration, $\bar{N}_v$ [a]	Stability (ref. 15)	Alloy	Average electron vacancy concentration, $\bar{N}_v$ [a]	Stability (ref. 15)
Inconel X-750	1.60	Stable	Mar-M 200	2.41	Stable
Nimonic 80	1.73	↓	B-1900	2.42	Stable
Inconel 600	1.77		IN 100	2.43	Sigma
Nimonic 90	2.03		René 41	2.46	Mu
Waspaloy	2.09		Udimet 500	2.47	Sigma
Alloy 901	2.23	Mu	PDRL 163	2.52	Sigma
Nicrotung	2.25	Stable	Mar-M 246	2.53	Stable
Inconel 700	2.27	↓	Unitemp 2-1D	2.53	Stable
Inconel 718	2.29		Nimonic 115	2.53	Sigma
UnitempAF 1753	2.30		TRW 1900	2.54	Stable
Unitemp 2-1DA	2.36		Alloy 713C	2.56	Sigma
M 252	2.36		Udimet 700	2.57	↓
Udimet 520	2.37		IN 728 NX	2.75	
René 85	2.39		TRW 1800	2.76	

[a]

$$\bar{N}_v = \sum_{i=1}^{n} \left(N_{v_i}\right)(\text{atom fraction})_i$$

where

$N_{v_{Ni}} = 0.61$ (ref. 1)

$N_{v_{Co}} = 1.71$ (ref. 1)

$N_{v_{Fe}} = 2.66$ (ref. 1)

$N_{v_{Cr}} = 4.66$ (ref. 1)

$N_{v_{Mo}} = N_{v_W} = 9.66$ (ref. 16)

$$\left.\begin{aligned} N_{v_{Al}} &= 7.66 \\ N_{v_{Ti}} &= 6.66 \\ N_{v_V} &= 5.66 \end{aligned}\right\}$$

Where N_v has not been reported, it is assumed to be 10.66 minus the element's group number.

chemistries reported by Collins and Kortovich in reference 15, because the stability of these alloys when exposed to 1600° F (871° C) for 1500 hours was reported in the reference.

Several values of N_v for Mo and W were used in an effort to empirically find a computation capable of separating stable and unstable alloys. The range of $N_{v_{Mo}}$ was 4.66 to 10.5 and N_{v_W} was varied from 4.66 to 9.66. An example of the results of these calculations is shown in table IV.

In all cases tried, if a critical $\bar{N}_v$ was selected such that all alloys which form mu or sigma have a higher $\bar{N}_v$ than $\bar{N}_{v_{crit}}$, then some stable alloys also had values of $\bar{N}_v$ higher than $\bar{N}_{v_{crit}}$. Conversely, if $\bar{N}_{v_{crit}}$ was selected such that it was greater than the highest $\bar{N}_v$ of all stable alloys, then alloys which form sigma or mu were found at values lower than $\bar{N}_{v_{crit}}$. It is noted, however, that, if a lower bound for sigma or mu formation is selected, most of the "stable" exceptions (i.e., Mar-M 200 and B-1900) have been reported to form acicular carbide phases. Further, if a lower bound for sigma is established, the stable exceptions contain in excess of 5.0 weight percent W. Because the proposed method does not predict W accurately, it might be assumed that the stability prediction problem results from this inability to properly account for W. However, sigma has been observed (ref. 16) in the Alloy 713 family (which is free of W) at lower $\bar{N}_v$ levels than the lower bound shown in table IV. This tends to indicate that the prediction problem may have its source in the $\bar{N}_v$ model itself.

CONCLUDING REMARKS

An analysis using analytic geometry to assist in the interpretation of two-phase regions in multicomponent phase diagrams has been presented. This analysis when used with "phase computation" procedures is capable of estimating the composition of the gamma phase in nickel-base superalloys with reasonable accuracy compared to published data for the gamma phase.

The underlying principles of the analysis proposed are valid in a two-phase region of any multicomponent system because the tie line is a straight line and solvus hypersurfaces can be expressed mathematically. The problem is one of obtaining data and deducing a parametric expression for the tie lines.

I believe the technique can be applied with even better accuracy as more information on the phase relations in the superalloy system become available. This will permit reducing the number of assumptions used in the calculation described in this report.

The application of the average electron vacancy concept to the computed gamma analysis does not allow prediction of intermetallic compound formation with reliability (when applied to a broad spectrum of alloys). It appears to me that this is in part due to inadequacies in the N_v model itself. This model assumes that the gamma solubility limits relative to sigma, mu, and so forth are functions only of N_v and ignores atomic size effects and electronegativity effects. Further, the model assumes that the elemental N_v can be deduced by location in the periodic table and perhaps empirically from simple phase diagrams. The N_v model also assumes that the N_v is the simple arithmetic average of the elemental N_v and is independent of the matrix. In other words, it assumes no elemental interactions take place.

If a unified system of predicting alloy stability is to be developed, it requires both a method of estimating phase relations in multiphase systems and an adequate solid state physics model. The work described here is intended to further our ability to estimate the phase relations. It is, however, only a preliminary approach and its ultimate refinement requires substantially more data on the superalloys system.

In closing, then, it should be recognized that where element partitioning data for an alloy, such as that in reference 13, is available, that data should be used in preference to the proposed estimating procedure.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, February 10, 1970,
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