PHACOMP REVISITED

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Abstract

One of the most interesting metallurgical advances of recent years is the computerized PHACOMP system for control of nickelbase alloy composition. This paper begins with a brief review of the fundamental and calculational basis for PHACOMP. demonstrates the iterative process by which PHACOMP has extended our knowledge and understanding of the important Ni-Cr-Co-(Mo.W) alloy matrix system (the basis of most nickel-base superalloys) and explains why a unique, single-valued function of the critical PHACOMP "breakpoint" is not really possible. This realization in turn, has allowed PHACOMP to be applied in an ever-broadening. more successful role. With the aid of quaternary and psuedoternary diagrams and with input from the original PHACOMP system, specific examples of Ni - and Co-base superalloys are used to demonstrate the use of average-electron-hole values for critical "breakpoints." Alloy composition and phase reactions are the hases for these predictions. Thus, an alloy designer and user can both benefit from a standardized calculation system, using predetermined breakpoints, without resorting to artificial modification of individual element electron-hole coefficients.

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Introduction

PHACOMP is a computerized calculation technique which predicts the tendency for an austenitic alloy to precipitate the intermetallic compounds usually identified as TCP phases. These phases include at least 0, μ , R, χ , and also Laves. Since the basic tenents of PHACOMP are founded on atomic electron vacancy (electron hole) theory, the system is at present, limited to these particular types of phases, all of which are electron compounds, or at least, as in the case of Laves, electron bonding plays a strong role (1,2). Such phases are characterized by a narrow, rather specific, range of electron-to-atom ratios (1).

Present interest in the use of the PHACOMP tool is prompted by the experience that the formation of σ , μ , Laves and the like in commercial high-strength high-temperature alloys usually produces embrittlement and loss of ductility, a significant reduction in rupture strength, or some combination of properties which seriously degrade performance. Although these specific effects, and the properties of the TCP phases themselves are of considerable practical and scientific importance, it is not the purpose of this paper to explore these areas. Rather, it is the present objective to penetrate and uncover as much of the more fundamental aspects of the PHACOMP calculation tool itself as is possible at this very early stage of its development, and - of more immediate importance - to describe meaningful ways of applying the tool to alloy systems which, in the first full flood of its use, appeared to be exceptions to the general case.

Thus, while detailed discussions of specific mechanical, morphological, and metallographic characteristics and effects of the electron compounds are generally ruled out for discussion here, several introductory points should be made. For instance, phase morphology of the TCP phase may affect one property more than another. As an example, σ has been seen in both platelike and in blocky form. In the blocky or globular condition, its morphology may not be directly conducive to loss of ductility and it would not be expected to generate easy paths for alloy fracture; platelike σ , when it occurs, does produce these effects. On the other hand, both types of σ will tend to tie up important refractory metal and other atoms in the alloy, rendering such elements much less effective as strengthening participants. Undoubtedly, μ , χ , and Laves behave similarly.

Since PHACOMP is a vehicle to predict the presence or absence of certain phases in an alloy structure of presumably known chemistry, it in a very real sense, replaces important, selected regions of phase diagrams, particularly those diagrams with three or more components where lack of experimental information or an inability to visualize and understand multi-dimensional phasespace confounds us. Thus, in this realm, PHACOMP is a demonstration of contemporary artificial intelligence. It substitutes

mathematical mapping and computation to, firstly, fix the position of the γ vs. (γ + σ) or (γ + σ) vs. σ phase boundary and, secondly, to locate an alloy with respect to this boundary. γ , herein, is understood to represent the fcc solid-solution matrix (austenite), characteristic of alloys such as AISI 310 or Udimet-700, from which σ -phase can be generated. Instead of σ , of course, μ , χ , or Laves might be the generated phase, depending on the austenite composition.

The discussion below will review the history and theory of PHACOMP in sufficient detail that the successes and failings of PHACOMP may be better understood. Included also is considerable speculation on both the theoretical bases for PHACOMP, and on the reasons for the effects of various alloying elements. No apology is made for this, but it is hoped that sufficient disagreement will be stirred to provide refutation or substantiation of the speculative arguments. Much of the discussion will surround o, since most of the theory and investigation has involved that phase. Some familiarity with the "modern" PHACOMP/electron vacancy theory (3,4,5) is assumed.

Blectron Vacancy Numbers

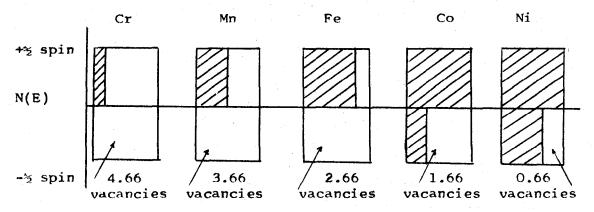
Almost 30 years ago Pauling (6) combined theory and experimental observation to provide a coherent explanation of magnetic properties of the first long period transition elements Cr, Mn, Fe, Co and Ni. The electronic structure of these atoms is presented in Table I, together with their Goldschmidt atomic diameters.

			TAB	LE I					
Element	Atomic No.	ls	2s	sp	3s	3p	3d	4 s	o Diameter-A
Bremeire	recourse 140.	1.5	23	<u> </u>		<u> </u>	<u> </u>	45	Diameter-A
Cr	24	2	2	6	2	6	5	1	2.57
Mn	25	2	2	6	2	6	5	2	
Fe	26	2	2	6	2	6	6	2	2.54
Co	27	2	2	6	2	6	7	2	2.50
Ni	28	2	2	6	2	6	8	2	2.49

It is characteristic of transition elements that the 3d shell, which could accept 10 electrons, remains only partially filled while some of the electrons have already occupied the 4s orbital. Further, atomic diameter varies only about three percent in proceeding from Cr to Ni.

Pauling interpreted these facts as meaning that the five d-orbitals of each spin could be divided into 2.44 non-bonding orbitals and 2.56 bonding orbitals. The latter orbitals could

hybridize with p- and s- orbitals to account for metallic bonding. The 2.44 d-orbitals not required for bonding are then available to participate in other events. Pauling extended his argument by assuming that Cr requires 5.78 hybrid (spd) electrons for bonding. Since six are available in the 3d, 4s orbitals, 0.22 electrons must be "left over." These electrons occupy the 3d non-bonding orbitals, taking up parallel spins so long as possible. Extending this on to Mn, Fe, Co and Ni, Pauling assumed that the constancy of atomic diameter indicated that the number of spd bonding electrons remained constant at 5.78 with an increase in non-bonding electrons to 1.22 for Mn, 2.22 for Fe, 3.22 for Co, and 4.22 for Ni. He then arrived at the following density of states diagrams for non-bonding 3d orbitals, the positive spin positions being occupied first;

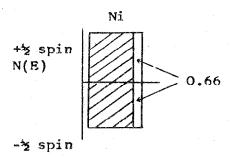


In the case of Co, as for Ni, vacancies are matched by unpaired electrons. In the cases of Cr, Mn, and Fe all non-bonding electrons are unpaired. The correct physical term for these "vacancies" is now "electron holes." This document will use the terms interchangeably to aid in the transition for metallurgists.

Atomic theory predicts that the magnetic moment at absolute zero should be equal to the average number of unpaired electrons. For Fe, Co, and Ni the magnetic moments have been measured. The moment for Fe is 2.22 μ_B , for Co 1.71 μ_B , and for Ni 0.61 μ_B , in close agreement with the Pauling predictions of 2.22, 1.66, and 0.66.

Assuming, at least for the moment, that Pauling's average electron vacancy numbers are correct, we might consider the effect of temperature on electron vacancies. Kittel (7) has shown the difference in electron density of states at 0 K and above the Curie temperature for Ni. At absolute zero Kittle's diagram is essentially that shown above, excepting that Kittle corrects the magnetic moment for orbital electron motion, and, thus calculates only 0.54 electron vacancies (unpaired electrons). Above the Curie temperature, thermal effects redistribute the vacancies or holes between + spin and - spin to yield zero net magnetic moment.

The density of states might be diagrammed as below.



Note that the number of unpaired electrons is now zero, but the number of 3d electron vacancies is unchanged. That is, there is no effect of temperature on the average electron vacancy number.

It is difficult, in quantitative terms, to extend the electron vacancy numbers to elements other than Cr, Mn, Fe, Co and Ni. One can assume that vacancy numbers (N_v) are constant within a periodic table group; for instance, that N_v for W=Mo=Cr=4.66 in Group VI. This approach is often followed. Besides the absence of 3d vacancies upon which Pauling built his argument, Hume-Rothery (8) has pointed out that the compressibility of Cr is 0.6, that of Mo is 0.36, and that of W is 0.3 and that this must mean stronger bonding in W than in Mo than in Cr. This is taken to mean (9) that the <u>effective</u> valence of Cr is less than that of Mo or W. The electron hole numbers should then be greater for Mo and W than for Cr. This may be a general trend for Groups VIA, VIIA, and VIII, N_v increasing with increasing period. Quantifying this approach from theory does not now appear possible.

Handling Group IIIB, IVA, and VA elements of alloying interest is even more difficult. About the best that can be done is to assign these elements an $N_{\rm V}=10.66$ - GN where GN is the Group Number. This at least gives numbers consistent with Pauling's approach. Fortunately, Group IIIB, IVA, and VA, elements rarely participate in solid-solution roles in alloys of interest.

Electron Vacancy Theory Applied to Alloy Phases

In 1951, Rideout, et al, (10) explored 1200C isotherms of the Cr-Co-Ni, Cr-Co-Fe, Cr-Co-Mo, and Cr-Ni-Mo ternary systems. At this temperature, extended regions of σ -phase were formed in the four ternary systems. Sully and Heal (11) had previously suggested that σ was an electron compound. Rideout and Beck, (10) hypothesized that it should be possible to characterize the range of σ composition by an average electron vacancy number $(\overline{N}_{\rm V})$ of the solid-solution matrix which could be expressed by a linear combination of terms as:

$$\overline{N}_{V}$$
 = 4.66 (Cr+Mo) + 3.66 (Mn) + 2.66 (Fe) + 1.71 (Co) + 0.61 (Ni) (i)

where the elemental symbols represent the atom fraction of corresponding element in the alloy and the numerical multipliers are Pauling's electron vacancy numbers. The range of 0 compositions were characterized by $N_{\rm v}$ values from 3.16 to 3.66 when calculated by formula (i). After plotting iso-vacancy lines, these investigators found that better agreement between iso-vacancy lines and 0 fields was achieved using an $N_{\rm v}=5.6$ for Mo, even though no theoretical basis existed for assigning the numerical value. The $N_{\rm v}$ formula became

$$\overline{N}_{V} = 5.6(Mo) + 4.66(Cr) + 3.66(Mn) + 2.66(Fe) + 1.71(Co) + 0.61(Ni).$$
 (ii)

This formula narrowed the range of \overline{N}_{V} values to 3.35 - 3.68, apparent evidence that σ itself can be treated by electron vacancy theory.

Rideout et. al. (10) considered the Cr-Mn o-phase investigation of Pearson, Christian, and Hume-Rothery (lla) and concluded that Mn must be assigned an $N_{ij} = 3.3$, instead of Pauling's 3.66, to achieve agreement with their work. Further consideration of Martens and Duwez (12) work on the 1290F Fe-V-Cr system shows that o extends in a band from V to Cr at a constant average atom fraction Fe. This would suggest $N_{f v}$ for V equals $N_{f v}$ for Cr (4.66?). Based on this assumption, Rideout, et al (10) calculated Nv values for the Pearson, et al (11), V-Co, V-Ni, and V-Mn ophases. They found good agreement with their own work (10) if the Mn N_v was again assumed to be 3.3. Poorer agreement was noted in the V-Co ($N_V = 2.83-3.24$) systems, the N_V values being too low. Correction would seem to require an increase in Co, Ni, or V N., values. A critical look at Martens and Duwez (12) Fe-V-Cr diagram substantiates the conclusion that the average atom fraction Fe remained constant as V substituted for Cr in σ_{ullet} However, the slope of the α Fe vs. (α Fe + σ) boundary is not zero, but shows more Cr in σ at the Fe-Cr side than V at the Fe-V side. Fe's $N_{f V}$ value is assumed constant, $N_{f V}$ for ${f V}$ must be greater than N_V Cr. Calculation of an N_V for V on this basis (assuming 2.66 for Fe and 4.66 for Cr) yields a value of 5.06. Using this value for the V-Co system would provide agreement with Rideout's work, but it is insufficient help in the V-Ni system, N, is still too low. N., for Ni must be greater.

Greenfield and Beck (13) have justified two values of $N_{\rm V}$ for V-5.66 with Ni and Co, or 4.88 with Mn or Fe. Their reasoning was that V with only 5 3d electrons, has 5.78-5.00 = 0.78 unfilled bonding orbitals coupled with 4.88 non-bonding (2.44 of each spin) for a summation of 0.78 + 4.88 = 5.66 electron vacancies possible. However, they believe that paired electrons in Ni and Co will help fill the 0.78 unfilled V bonding orbitals leaving an effective 5.66 vacancies attributable to V in the V-Ni-Co combination. However, in combination with Fe or Mn (and presumably Cr), which have no paired 3d electrons, only the 4.88 non-bonding orbitals

are accountable as vacancies for V. From forced fitting of Marten's and Duwez (12) Fe-V-Cr diagrams and from Greenfield and Beck's theorizing, it appears that the N_V for V is compositionally dependent.

Das, et al, (14) continued the work of Rideout, investigating 1200C isotherms of Mo-Fe-Co, Mo-Fe-Ni and Mo-Ni-Co. Application of electron vacancy theory to these u-forming systems led to forced N, values of 2.2 for Fe (equal to the magnetic saturation moment) and 1.6 for Ni (no apparent theoretical basis). These values also gave better fits for Rideout's o work. As in Rideout's work (10) N, for Mo was assumed to be 5.66. In discussion, Das considered the (Co, Mo) v, concluding that an N_v of 4.66 for Mo gave a more acceptable No for Mo. These workers than hypothesized that the effective N_v for Mo is equal to that of Cr except when Mo and Cr occur together in the same alloy. Then, if the amount of Cr is greater than that of Mo, Mo contributes more (5.6) vacancies. A similar conclusion could probably be drawn regarding the effect of W in a Cr-containing alloy; even a greater N, contribution might be made if both W and Mo should occur in an alloy with Cr. Again, as for V, the N, for Mo (and probably W) seems dependent upon composition.

Greenfield and Beck (15) lend additional support to compositional dependence of $N_{\rm V}$ values. Their results show that Cb and Ta should have equal $N_{\rm V}$'s, since both Cb and Ta form σ at 40 atomic percent Rh. This argument was confounded when they looked at the Pt-Cb and Pt-Ta σ -phases where σ occurs at distinct-ly different atom fractions of Pt for Cb and for Ta. Thus, there may be a general compositional dependence of $N_{\rm V}$ values.

Application of Electron Vacancy/PHACOMP Theory To Engineering Alloys

In the above sections we have included results and commentary thereon of electron vacancy theory and its application, in a rather scientific sense, to the correlation of phase studies in relatively simple solid-solution alloys. It was not until 1963-64 that apparent effort was made to apply electron hole theory to the prediction of v-phase in complicated, engineering alloys. Two apparently independent and virtually simultaneous attacks were made by Boesch and Slaney (3) at Special Metals Corporation and by Woodyatt, Sims, and Beattie (4) at General Electric. The two approaches differed from each other, but differed from previous applications even more significantly as described below.

First, the work of Rideout, Das, Greenfield and Beck had as its objective the prediction of an N_v for pure σ -phase field or, at least, the σ vs. $(\sigma + \gamma)$ phase boundary. It is important in an engineering alloy to predict not the σ vs. $(\sigma + \gamma)$ boundary but the γ vs. $(\gamma + \sigma)$ boundary. The question we must answer is "will we form any σ from our essentially γ alloy?" not "Will we form all σ from our γ + σ alloy?" Since it is σ which

is the electron compound, not γ , no theoretical basis exists for predicting the γ vs. $(\gamma + \sigma)$ boundary by electron vacancy theory unless the γ vs. $(\gamma + \sigma)$ boundary lies parallel to the $(\gamma + \sigma)$ vs. σ boundary. As we have seen, electron vacancy theory may apply to this latter boundary. If such parallelism is the case, as it fortunately generally is, then the γ vs. $(\gamma + \sigma)$ boundary will be a line of constant electron vacancy, but displaced to a lesser numerical value than the 3.4 to 3.6 N values of Rideout (10) for pure σ . If parallelism does not exist between the two boundaries of the $\gamma + \sigma$ field, we are confounded. If the iso-electron vacancy line does not track the σ vs. $(\gamma + \sigma)$ boundary, we are confounded even with parallelism of the boundaries. If the boundaries are convergent but the iso-electron vacancy line tracks the γ vs. $(\gamma + \sigma)$ boundary, we can use the technique to predict sigma-prone alloys, but we have no theory!

Secondly, many alloys of interest, particularly the high-temperature nickel-base alloys, are exceedingly more complex than simple solid solutions. Elements added at melting are not homogeneously distributed but, aside from casting segregation, are reacted and partitioned to form borides, varying carbides, and intermetallics such as γ' [Ni₃ (Al, Ti, Cb, Ta)]. Thus, the γ matrix from which σ (or μ or χ or laves) forms is not represented by melt chemistry, but differs significantly. We must either chemically analyze (extremely difficult in Ni-base alloys even if possible) or calculate (based on fact or judgment) the residual alloy matrix composition.

Boesch and Slaney (3) applied electron hole theory to control of sigma formation in the complex carbide, y', and solid-solution strengthened Ni-base alloy Udimet-700. Aware of the work described above, they implicitly assumed that o would form from the They further assumed that carbide depletion of residual matrix. the matrix could be ignored at the low ($\approx 0.05\%$) C levels in U-700 and that the residual matrix composition could be well approximated by depletion of the melt chemistry by those elements forming y'. For No values Boesch and Slaney relied upon the Pauling/ Rideout/Beck coefficients of 4.66 for Mo and Cr, 1.71 for Co, and 0.61 for Ni and calculated an averaged electron vacancy number for the residual matrix. Since Boesch and Slaney were interested in producing an alloy free of sigma, an \overline{N}_{V} value was needed to track the γ vs. $(\gamma + \sigma)$ phase boundary or one which lay wholly within the y field. A source for the latter value lay in Udimet-500 which had an $\overline{N}_v = 2.32$ and had not formed σ in a 1600-hour rupture test. Armed with this upper, safe value, Boesch and Slaney made the first known industrial application of electron vacancy theory to the control of o-phase in an engineering alloy. At the present writing, no case is known in which diligent application of the Boesch/Slaney system has failed to provide σ-free U-500 or U-700.

As noted above, Woodyatt, et al (4) had also been following an electron vacancy approach to phase computation (PHACOMP). Their

approach was far more general and searching than Boesch and Slaney's, yet quite similar in some respects. Woodyatt's (4) efforts were directed toward achieving a system for predicting ofree or o-prone structural alloys from among the common hightemperature alloys, whether they be steels or superalloys. values were in the main, set at 0.61 for Ni, 1.71 for Co, 4.66 for Cr, Mo and W, 3.66 for Mn, 2.66 for Fe; variations with Ni at either 0.61 or 0.66 and Fe at 2.66 or 2.22 were also studied. Perhaps the most technically significant difference between Woodyeatt, et al, and the Boesch/Slaney work is the consideration of all phases in the former approach. Accounting was made for depletion of the melt chemistry due to formation of borides, monoand complex carbides, and y'. Much of this was based on the phase studies, both published and unpublished, of H. J. Beattie. Then, a PHACOMP model was established to include both order of expected phase formation and compositions of the phases formed. This model has continuously undergone change as additional evidence and conjecture have been brought to bear.

Woodyatt et al (4) applied this model to 12 compositionally similar Udimet-700 heats, heats which both did and did not form No values ranged from 2.32 to 2.67 with a clear, discernible break near $N_{ij} = 2.52$. At greater N_{ij} values, σ formed. At lesser values no o was found. Later improvement_of computer arithmetic has resulted in the break or "just-safe" N, being set at 2.49, but disposition of the various heats remains unchanged. Application of the Woodyatt/Sims/Beattie technique to U-500/U-700 heats has also successfully predicted o-prone and o-free heats, and is in general commercial use. Application (4) to a wide variety of stainless steels and nickel-base superalloys has also provided proper disposition. The wide application has provided added benefit, since it has been found that μ , χ , or Laves-forming alloys appear to form at N_v values greater than 2.30, provided μ , x, or Laves-forming elements are present. This phase boundary is not so well located as the γ vs. $(\gamma + \sigma)$ boundary, however.

Problems With PHACOMP

Several problems have been encountered with application of The first of these is easily solved with a little thought. PHACOMP is both a technique and procedure for application of electron vacancy theory. Certain rules have been laid down (4) as to order of phase precipitation and phase composition to facilitiate general calculation of N_v. The rules are based on general, typical, usual behavior and construction of allow phases in nickel-base superalloys. However, some alloys may deviate from these rules more markedly than the average. For instance, Udimet-520 with more than 6.1% Mo + W forms M23C6 carbides, not M6C as is the general case with such a Mo + W content. Thus, rather than rote application of rules, the PHACOMP calculation must account for actual phases formed in arriving at N... That is, the first problem with PHACOMP does not lie in PHACOMP. but in the user and the veracity with which he knows and applies

alloy phase information. \overline{N}_v values, as closely as possible, must reflect reality - reality in identification and composition of the phases present. To this end, it is obvious that more detailed knowledge is required of the exact composition of precipitating phases. Without this knowledge, PHACOMP application will be beset by errors and exceptions.

The second problem is more troublesome. Some Ni-base alloys (INCO-713C and certain experimental alloys) have formed σ -phase at \overline{N}_{v} values significantly less than "known" safe values; conversely, some alloys had an unsafe \overline{N}_{v} but did not form σ . We will discuss - perhaps describe is a better word - some of these exceptions to PHACOMP, not because we conclusively know the cause of their deviation but rather to lay some foundation for that which follows.

Compositions of 713C, U-700 and alloys B, C, D, and E are listed in Table I. They have been presented in three ways - heat analysis in weight percent, heat analysis in atomic percent, and residual matrix composition in atomic percent following the Woodyatt/Sims/Beattie calculation procedure with the exception that Decker and Bieber's (16) precipitate compositions were used for 713C. Woodyatt, et al, $N_{\rm V}$ are also listed, as well as $N_{\rm V-SS}$. Heat analysis compositional variations, both by weight or atom fraction, are sufficiently obvious to require no further amplification.

INCO-713C is the only cast alloy of the four. Sigma phase occurrence has been reported in the alloy at $N_{\rm V}$ values <2.20. In view of the many successes of PHACOMP, this deviation seems difficult to reconcile. However, regardless of the general application intent in development of PHACOMP, the alloys studied have been principally those with residual matrices on or close to the Ni-Cr-Co ternary diagram (Fig. 1). On this ternary, the iso-PHACOMP lines are roughly parallel to the γ vs. (γ + 0) boundary. As noted previously, parallelism is a requisite for PHACOMP application. INCO-713C does not intentionally contain Co; thus its residual matrix does not lie on or close to the Ni-Cr-Co ternary (Table 1). The composition lies on or close to the Ni-Cr-Mo ternary shown in Figure 2.

Two residual compositions for INCO-713C have been plotted from Table 1 on Figure 2. These compositions formed 0 at \overline{N}_V values below 2.49. Two facts are immediately evident from consideration of the Ni-Cr-Mo ternary upon which the compositions are plotted. First, iso-PHACOMP lines are not parallel to the 2200F γ vs. (γ + 0) boundary, but intersect it at approximately 30°. Furthermore, the 2.49 iso-PHACOMP "just-safe" line is neither "just-safe" nor conservative. Sigma should and readily will form at \overline{N}_V values less than 2.49 because PHACOMP does not predict the Ni-Cr-Mo diagram γ limit with even possible accuracy. This points out the inherent danger present in trying to make a Ni-Cr-Co-Mo (e.g. IN-100) "safe" by reducing Co.

Second, if one constructs (merely by the use of a steady hand and good eye - no theory) a line parallel to the two-phase boundary at $\overline{N_V}$ - 0.2 commencing at the phase boundary intersection with the Ni-Mo and Ni-Cr binaries, the plotted INCO-713C composition are close to being o-prone, (as alloy #1 was prone). Construction of the line was performed at an $\overline{N_V}$ = 0.2 less than the phase boundaries by analogy with the 1200C Ni-Cr-Co ternary, (Fig. 1). The "just-safe" value on that ternary is \approx 0.2 less than the phase boundary $\overline{N_V}$ opposite "just-safe" U-700's composition, Table 1 and Figure 1. This is admittedly an unrefined, rather coarse procedure; but its logic when viewed in the matrix of the ternary phase diagram is difficult to refute.

Moreover, this seems such a simple solution to account for 713C's apparently anomalous behavior that we have followed it one more step. As we have been successfully doing on the Ni-Cr-Co ternary, we would like to be able to calculate an $N_{\rm V}$ for 713C above which σ will form and below which σ will not form. An equation for the constructed line, parallel to the two phase boundaries, can easily be solved if we assume, for convenience, that $N_{\rm V}$ for Ni = 0.61, $N_{\rm V}$ for Cr = 4.66, and $N_{\rm V}$ = 2.49. We have, then,

$$\overline{N}_{v} = 2.49 = 0.61 \text{ Ni} + 4.66 \text{ Cr} + N_{v} \text{ Mo}$$
 (iii)

where the elemental symbols represent atom fractions. Using the binary intercepts of the previously constructed line, N_v for Mo is found to have a value of approximately 10. Thus, N_v would be expressed, in the general case, as

$$\overline{N}_{v} = 0.61 \text{ Ni} + 4.66 \text{ Cr} + 1.71 \text{ Co} + 10 \text{ Mo}.$$
 (iv)

But the solution is not so neat as first appears. The difficulty lies in two places. First, if we apply $N_v=10$ for Mo to another alloy, "just-safe" U-700, the critical break-point N_v is shifted upward to 2.70. Since it was set equal to 2.49 in the determination of $N_v=10$ for Mo, we have what is analogous to a closure error in land surveying. What has really been done in that we have attempted to define an iso-PHACOMP plane in quaternary space. The basic problem of defining as iso-PHACOMP plane in this manner is that the four two-phase boundary/binary leg intercepts do not all lie on a plane surface and even a "best fit" would involve shifting all coefficients.

A practical approach might seem to be to ignore the apparent closure error and to maintain that INCO-713C can be properly disposed of with $N_{\rm v}=2.49$ and $N_{\rm v}$ for Mo = 10. This is an acceptable solution provided that we can demonstrate, first, that σ -prone heats will be predicted as σ -prone and, second, that σ -free heats will be predicted to be σ -free. The first requirement has been demonstrated previously. The second demand cannot be satisfied with the limited 713C information available. INCO has found heat 1 (Table 2) to be σ -prone yet plotting its residual matrix composition in Figure 2 (or calculating its $N_{\rm v}$) would predict no

o. Thus, we do not really seem to be able to quantitatively dispose of INCO-713C, although qualitatively we realize its closeness to the γ + 0 boundary. A random proliferation of calculation systems by arbitrary adjustments of coefficients or assumptions of phase reactions is, thus, to be guarded against since it only further clouds the real problems.

We can, of course, cite a number of factors which could confound meaningful PHACOMP analysis of INCO-713C. For instance, heat chemistry (particularly elements such as Mn and Si which were not reported), σ -forming conditions (time, temperature, stress), and details of phase identification are neither clearly nor definitively known to us since a variety of alloy, tests, and data sources apparently account for the 713C information. Also, an alloy with a nominal composition near the phase boundary (713C) is more likely to be influenced by minor variations in chemistry. Nonetheless, our inability to quantitatively dispose of INCO-713C remains disturbing.

The experimental alloy C's composition and \overline{N}_V have shown anomalies with respect to PHACOMP behavior, forming σ at $\overline{N}_V=2.36$ while surrounded by B, D, and E compositions which did not form σ . This can be understood in terms of Figures 3 and 4. Rideout and Beck (10), in their investigation of the Ni-Cr-Co-Mo system, constructed 2200F γ -solution phase boundaries for constant Mo (iso-Mo) concentrations on the Ni-Cr-Co ternary. These boundaries are close to straight lines. After conversion to atom percent and with some liberties in making the boundaries straight, Rideout and Beck's (10) 2200F pseudo-quaternary is presented as Figure 3. Also, a 9 a/o Mo boundary has been interpolated onto the diagram. This kind of diagram is useful since residual (post-precipitation) matrix compositions can be plotted on it, allowing two dimensional visualization.

The residual matrix composition of "just-safe" U-700 (JS-U-700) has been plotted on Figure 3. It is, of course, clear that JS-U-700 with 5.2% residual Mo is predicted to be single-phase at 2200F, as experience has shown it to be. We do, however, know empirically that JS-U-700 lies approximately on the γ vs. ($\gamma + \sigma$) boundary at \$1600F. This knowledge can be combined with the 2200F, iso-Mo boundaries to construct a 1600F pseudo-ternary, This latter diagram has been constructed by moving the iso-Mo boundaries of Figure 3 downward to further restric: the y-The 1600F lines of Figure 4 have been mainsolid-solution field. tained parallel to the 2200F lines, but shifted downward, away from Cr, to place the 5%-Mo boundary through JS-U-700's residual matrix composition. The binary ends of the iso-Mo lines have not been completed since it is in these regions that cusps and irregularities are most likely to occur. Thus, knowledge gained from PHACOMP on a commercial alloy was combined with literature phase diagram data to yield a new pseudo-quaternary phase diagram.

With this background, we can return to consideration of alloys B. C. D. and B. The compositions of these alloys have been given previously in Table 1, in terms of overall melt composition and residual matrix composition. These residual compositions have been plotted on Figure 4 with the necessary simplifying assumption that an a/o of W is equivalent to an a/o Mo. is readily apparent that Alloy B (7 a/o W) lies on the "safe" or γ side of the γ -(γ + σ) boundary by comparison to the interpolated 7 a/o iso-Mo boundary. Similar considerations apply to Alloy D (5.2 a/o Mo) and Alloy E (5.6 a/o Mo + W) with respect to the 5 and 6 a/o iso-Mo boundaries. Thus, Alloys B, D and E would not be expected to produce o-phase from their residual matrix. did not generally form o, although occasional platelets may have been present in E. Conversely, Alloy C (9.02 a/o W + Mo) lies above (to the $\gamma + \sigma$ side) of the 9 a/o iso-Mo boundary. Thus, this alloy should form o. It did.

An even more important realization is implicit in the dia-The average-electron-hole breakpoint value is not singlevalued and unique but varies with the residual matrix composition (and, this of course, varies with temperature). To illustrate this, N, values have been used to label the ends of the 6% iso-Mo boundary, in Figure 4. Reconsideration of Alloys B, C, D, and E reminds us that Alloy C formed o while the others did not. was demonstrated above that this agreed with a constructed pseudoternary. To secure agreement with $N_{\mathbf{v}}$ values requires that the critical $N_{\rm U}$ value for each composition be calculated from the pseudo-ternary. This is done by calculating N, on the iso-Mo line characteristic of the alloy at its closest approach to that iso-Mo line. For instance, Alloy C's characteristic iso-Mo line is the 9% line, the alloy having ≈ 9 a/o Mo + W. The alloy composition most closely approaches this line at 40% Co, 33% Ni, 27% Cr. accounts for 91% of the alloy and must be adjusted to 36.4% Co, 30.0% Ni, 24.6% Cr, 9% Mo to account for Mo and 100% of the alloy. N, for this composition is:

$$\overline{N}_{v} = 0.61 \times \% \text{ Ni} + 1.71 \times \% \text{ Co} + 4.66 (\% \text{ Cr} + \% \text{ Mo})$$
 (v)

or

$$\overline{N}_{v} = 0.61 \times 0.30 + 1.71 \times 0.364 + 4.66 \times 0.$$
 336 = 2.36. (vi)

Thus, alloys of the generic composition of Alloy C should have a breakpoint of 2.36. Average-electron-hole values >2.36 should produce σ .

The same kind of reasoning can be applied to other alloys lying on this pseudo-ternary. For instance, we can take a typical cobalt-base alloy, MarM-509, and determine its \overline{N}_{V} breakpoint using the diagram. It has been found empirically in this Laboratory that Co-base alloys have higher breakpoint values - around 2.65-2.70 - than Ni-base alloys. This is readily apparent from Figure

4. It is instructive, however, to demonstrate calculation of MarM-509's breakpoint. The composition of MM-509 is given in Table 1. As done above for Ni-base Alloy C, the residual composition has been plotted on Figure 4. The characteristic iso-(Mo, W) line for MM-509 is the 2.0 a/o line. MM-509's closest approach to this line is at 63 a/o Co, 32 a/o Cr, 5 a/o Ni. The resultant \overline{N}_{V} after accounting for 2.1 a/o W is

$$\overline{N}_{v}$$
 = [+ 0.61 x 0.05 + 1.71 x 0.63 + 4.66 x 0.32] x
0.979 + 4.66 x 0.021 = 2.64. (vii)

Thus, we could expect σ formation in MM-509, or a similar alloy, at $N_V > 2.64$. Considering the general nature of the assumptions in PHACOMP, the agreement observed is reasonably good.

Summary

We have attempted to review the physical basis for PHACOMP, and to explain techniques for general application of the system. Obviously, PHACOMP is a computation tool in the developmental stages, and its use requires knowledge and judgment. Since PHACOMP attempts to simulate phase diagram information, it is important to note that iso-PHACOMP lines are not, in all cases, parallel to nor conservative with respect to γ vs. $(\gamma+TCP)$ boundaries. Complete solution to the problem will require more exact information on the composition and amounts of precipitating phases and matrix; more or better information is required on individual element N_{γ} values and their compositional variation. Nevertheless, in its present form with the techniques described above, PHACOMP can be used to maintain long-time microstructural stability in nickel and cobalt-base superalloys.

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TABLE I ALLOY COMPOSITIONS

		#1		7130	#3	"JUST-SAFE" U-70			
	<u>w/o</u>	<u>A/O</u>	A/O RESIDUAL	<u>w/o</u>	A/0	A/O RESIDUAL	W/O	A/0	A/O RE
В	0.009	0.05	•	0.011	0.06	•	0.03	0.15	
C	0.11	0.50	•	0.14	0.64		0.06	0.28	
A1	5.86	11.95	•	6.12	12.43	-	4.37	8.94	
Ti	0.79	0.91	-	0.71	0.81	-	3.40	3.92	
V	-	-	-	.		-	-	-	
Cr	13.23	13.99	28.86	13.30	14.01	29.76	14.60	15.49	31
Fe	0.10	0.10	0.22	0.18	0.18	0.42	_		
Zr	0.10	0.06	0.13	0.10	0.06	0.14	_		
Cb	2.09	1.24	••	2.08	1.23		- ·		•
Mo	4.46	2.56	3.68	4.52	2.58	3.74	4.45	2.56	5
Ta		-		•	_	-	. •		
M	-	-	-	-	•	· · · · · · · · · · · · · · · · · · ·	-		
Co	- 1,		· . •	-	•	_	17.6	16.48	-35
Ni	73.25	68,65	67.08	72.84	68.01	65.92	55.49	52.16	27
	•								
		พี.	, = 1.94			1.98			2.49
			,ss = 2.11			2.16			2.49
		๋	Present? Yes			No			No

TABLE I (Continued)
ALLOY COMPOSITIONS

	NULUI B				ALLOI C				ALLUY U			
	W/O	<u>A/0</u>	A/O RESIDUAL	w/o	<u>A/0</u>	A/C	RESIDUAL	W/0	<u>A/O</u>	A/0		
В	0.01	0.05	~	0.01	0.05			0.01	0.05			
Ç	0.13	0.62	•	0.12	0.57		- ,	0.12	0.55			
A1-	4.96	10.53	•	4.86	10.22		•	5.13	10.38			
Ti	3.90	4.66	•	3.83	4.54		-	3.88	4.42			
V	-			-	-			0.70	0.75			
Cr	9.80	10.79	25.33	9.80	10.69		24.13	12.00	12.59			
Fe	-		. •	•			-	-	-			
Z r	0.03	0.02	0.05	0.03	0.02		0.05	0.03	0.02			
Ср	-	-	·, •					_	-			
Мо	-	- ,	-	3.50	2.07		5.10	3.60	2,05			
Ta	-	· -	-	-				-				
W	8.70	2.71	7.04	5.10	1.57		3.95	•				
Co	15.10	14.67	39.62	14.90	14.34		36.98	15.10	13.97		:	
Ni	57.37	55.96	27.96	57.85	55.92		29.8	59.43	55.24		:	
									•			
		N	= 2.36			2.36	*			2.52		
		N _U	ss = 2.40			2.40				2.50		
			Present? No			Yes				No		

TABLE I (Continued)
ALLOY COMPOSITIONS

		ALLO	MAR -M509				
	w/o	A/0	A/O RESIDUAL	W/O	A/O		RESIDUAL
B	0.02	0.10	- -				
Č	0.24	1.09	•	0.6	3.00		•
Al	5.05		· .	•			•
Ti	3.77	4.28	_	0.2	0.25		- ,
v	0.70	0.75	1.00	_	÷		.
Cr	11,90	12.43	26.98	23.5	27.1		24.35
Fe	•			-	,==		-
Zr	0.03	0.02	0.05	0.5	0.33		0.27
Cb	_	-	. -	•		•	•
Mo	3.50	1.98	4.60	-	-	4.1	-
Ta	-		•	3.5	1.16		,
W	- ,		-	7.0	2.28		1.99
Co	15.10	13.92	37.11	54.7	55.66	* .	62.01
Ni	59.69	55.26	30.26	10.0	10.22		11.38
	•	_					e e e e e e e e e e e e e e e e e e e
		N _{vss} = o Present	2.35 2.33 t? No(?)			2.38 2.58 No	

