

CALCULATION OF MULTI COMPONENT PHASE DIAGRAMS FOR NIOBIUM ALLOYS

Larry Kaufman

140 Clark Road
Brookline, Massachusetts 02445-5848, U.S.A.

Abstract

The thermodynamic calculation of phase diagrams for binary, ternary and quaternary niobium alloys based on the Nb-Al-Cr-Ti system is illustrated over a wide range of temperatures and compositions. In addition Scheil Simulation of the freezing of quaternary alloys is used to show how the method can be applied in practice to anticipate segregation during casting of Nb alloys. Calculation of the Nb-Cr-Mo isotherm at 1200C shows how an "unexpected" miscibility gap, noted in the 1981 symposium could have been predicted. Finally, the current capability of using the CALPHAD method and the Thermo-Calc databases and software to extend such calculations to a wider range of multicomponent Nb alloys is considered.

Introduction

At the 1981 International Symposium on Niobium¹⁻⁴ an extensive survey of the properties of commercial Nb alloys was presented and related to the products and practice of that time. Argent¹ presented a wide ranging review of the existing information concerning binary and ternary phase diagram data derived from experimental studies of phase equilibria.

In the last 20 years many experimental studies of phase equilibria in multicomponent alloys have been done. Scientific papers covering such studies appear in the literature and handbooks and periodic reviews⁵⁻⁷ of binary and ternary niobium alloy systems have been published. These can be located by consulting the references noted above and other scientific sources. Notwithstanding the availability of such information the translation of such data for the commercial world of alloy synthesis and manufacture requires considerable art.

Most alloys contain more than three components and the data available does not always cover the manufacturing or use temperatures. To address such problems the CALPHAD Group was formed in the 1970's to deal with the task of calculating phase diagrams from thermochemical data^{8,9}. The availability of powerful PC's and the world-wide growth of "Computational Thermodynamics" for coupling thermochemical properties and phase diagrams of multicomponent alloys has yielded many examples of practical applications in recent years¹⁰⁻¹⁴. The Nb-Al-Cr-Ti system has been chosen below as an example for illustration by adapting the seminal work of Ansara¹⁵⁻¹⁸ to construct the database and derive Figures 1-5 for Nb-Ti-Cr and Ti-Al-Cr.

Calculation of the Binary and Ternary Phase Diagrams in the Nb-Al-Cr-Ti System

Figure 1 shows the calculated binary phase diagrams for the Nb-Ti, Ti-Cr and Cr-Nb systems as a function of temperature between 500C and 2500C and mole fraction between 0 and 1 for each of the components. The C15 and C14 phases are Laves phases. Figure 2 shows calculated isothermal sections in the Nb-Ti-Cr system at 1300C, 1500C, 1600C and 1800C.

Next the calculated binary phase diagrams for Ti-Al and Al-Cr are combined with the Ti-Cr binary to form the Ti-Al-Cr system shown in Figures 3 and 4. This system is more complex than that of the Nb-Ti-Cr system because additional binary and ternary phases are present. This complexity is evident in Figures 5-9 which illustrate other aspects of the Nb-Al-Cr-Ti database. For example Figures 3 and 6 show the Ti-Al α' (Ti₃Al) and γ (TiAl) phases as well as the TNAB β phase which contains Nb,Al,Cr and Ti. Finally the Al₂Ti and Al₁₇Ti₈ phases are included. The thermochemical properties of all of these phases are included in the database over temperature and compositions where they are stable, metastable and unstable. Figures 4 and 5 show that a Al₁₅Cr₄Ti₇ phase, called the tau phase¹⁷ is included in the database. This phase which is reported to exist over a range of composition is defined as in Figure 5 for simplicity. The extension of the C14 and C15 Laves phases into the Ti-Cr-Al ternary in Figure 5 has been derived from the abovementioned results of Ansara, Servant, Saunders, Shao, Tsakiroopoulos, Jewett and Dahms¹⁵⁻¹⁸. In this way the quaternary database is built up from the unary, binary and ternary thermochemical and phase diagram information and verified by experimental results drawn from various studies which were conducted over a wide range of conditions.

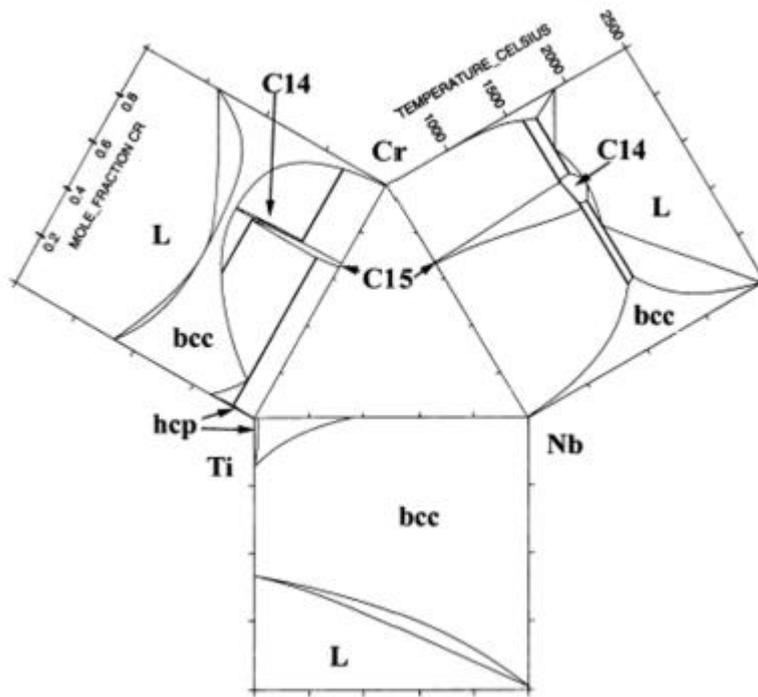


Figure 1: Calculated binary phase diagram components of the Nb-Ti-Cr system. The liquid phase is designated by L.

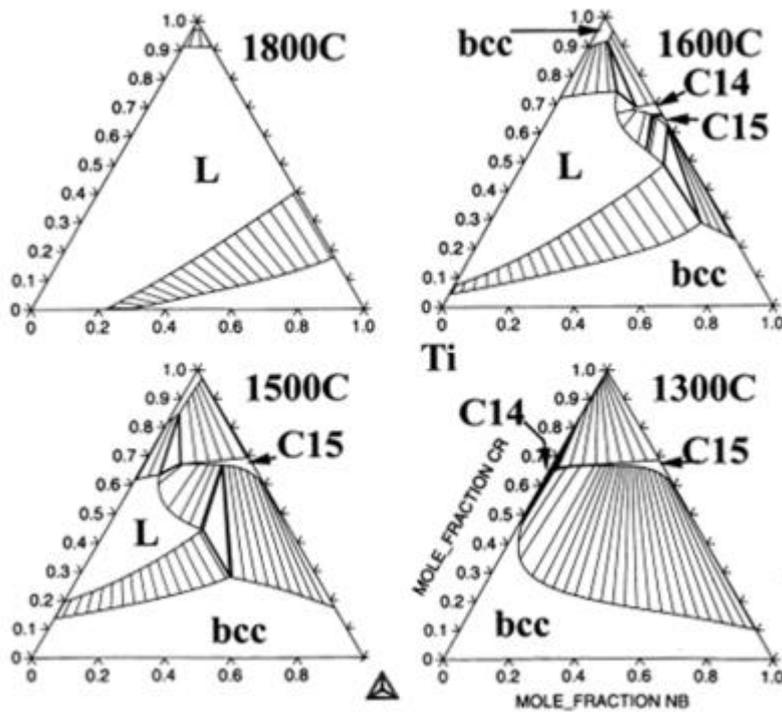


Figure 2: Calculated isothermal sections in Nb-Ti-Cr at 1800, 1600, 1500 and 1300°C. Two-phase regions are identified by tie-lines; three-phase regions by triangles and single phase regions are labeled.

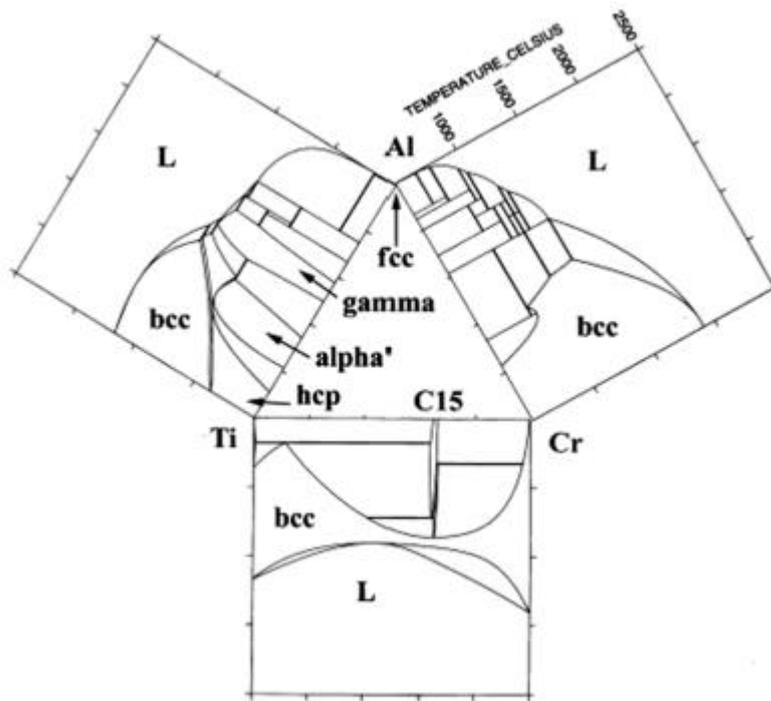


Figure 3: Calculated binary phase diagram components of the Ti-Al-Cr system. The liquid phase is designated by L.

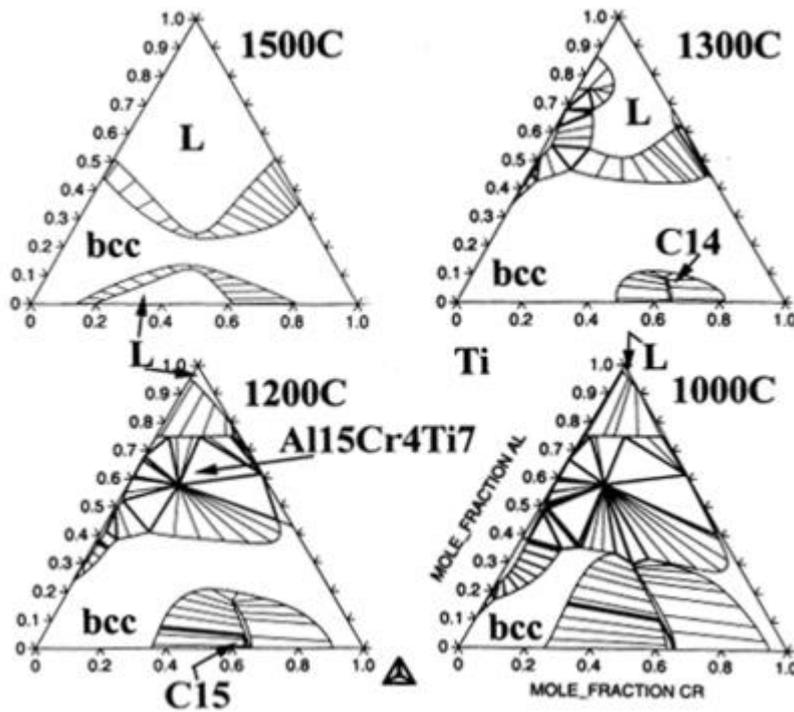


Figure 4: Calculated isothermal sections in Ti-Al-Cr at 1500, 1300, 1200 and 1000°C. Two-phase regions are identified by tie-lines, three-phase regions are identified by triangles and single-phase regions are labeled.

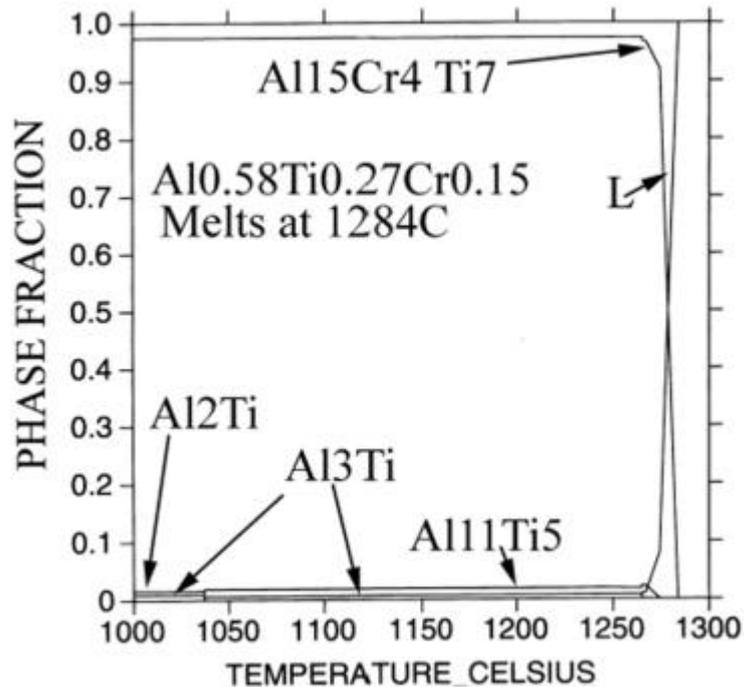


Figure 5: Calculated phase fraction vs. temperature curve for an alloy containing 27atomic%Ti and 15atomic%Cr (bal. Al).

Figures 6 and 7 display the combination of the Al-Nb binary with Ti-Al and Nb-Ti in Nb-Ti-Al adapted from the work of Servant and Ansara(15) showing the Nb₂Al(Sigma), Nb₃Al(A15) and Al₃NbTi₄ phases. The Nb-Al-Cr-Ti database describes the thermochemical properties of all of these phases.

Finally Figures 8 and 9 combine the Al-Nb and Al-Cr descriptions provided by Ansara^{15,16} with the Nb-Cr binary to generate the Nb-Al-Cr in keeping with the limited experimental results^{6,19}. The Al-Cr binary contains no less than eight compound phases as shown in Fig.8 including high and low temperature forms, Al₈Cr₅(H) and Al₈Cr₅(L), of the same compound phase.

Most of the phase diagrams shown in Figures 1-9 are of the classic type illustrating single phase fields and two and three phase equilibria in different regions of the composition versus temperature space. All of these diagrams are calculated assuming that equilibrium is attained. This may not be the case as the temperature is lowered. The methods used to calculate phase equilibrium from thermodynamic data can be readily applied in such cases by examining metastable equilibria where one or more phases, which would tend to form by diffusion controlled reactions, can easily be suspended and the resultant equilibrium can be recalculated for comparison with the "full equilibrium case".

Finally, it is possible to consider cases where diffusion is rapid in one phase (i.e. a liquid) but slow in a solid phase that coexists with the liquid leading to "Scheil Solidification" which can be used to simulate the levels of solute segregation encountered in the casting of alloys. Such calculations will be illustrated below for quaternary Nb-Al-Cr-Ti alloys. The exception to classic phase diagrams amongst the examples referred to above is Figure 5 which displays a calculated Phase Fraction versus temperature curve for an Al-Ti-Cr alloy containing 27 atomic percent Ti and 15 atomic percent Cr. This corresponds almost exactly to the ternary

composition of the $\text{Al}_{15}\text{Cr}_4\text{Ti}_7$ compound phase. Figure 5 shows that, above 1284C an alloy of such a composition is all liquid. As the temperature falls below 1284C the fraction of liquid falls rapidly from 1 as the fraction of the ternary compound rises from zero at 1284C to a value near unity. During the cooling a compound $\text{Al}_{11}\text{Ti}_5$ forms from the melt at 1275C, the liquid freezes and a third compound phase, Al_3Ti , forms at about 1263C. At 1040C the $\text{Al}_{11}\text{Ti}_5$ phase transforms into Al_2Ti and Al_3Ti . Thus this calculation can be used to trace the changes that occur when an alloy is cooled (or heated).

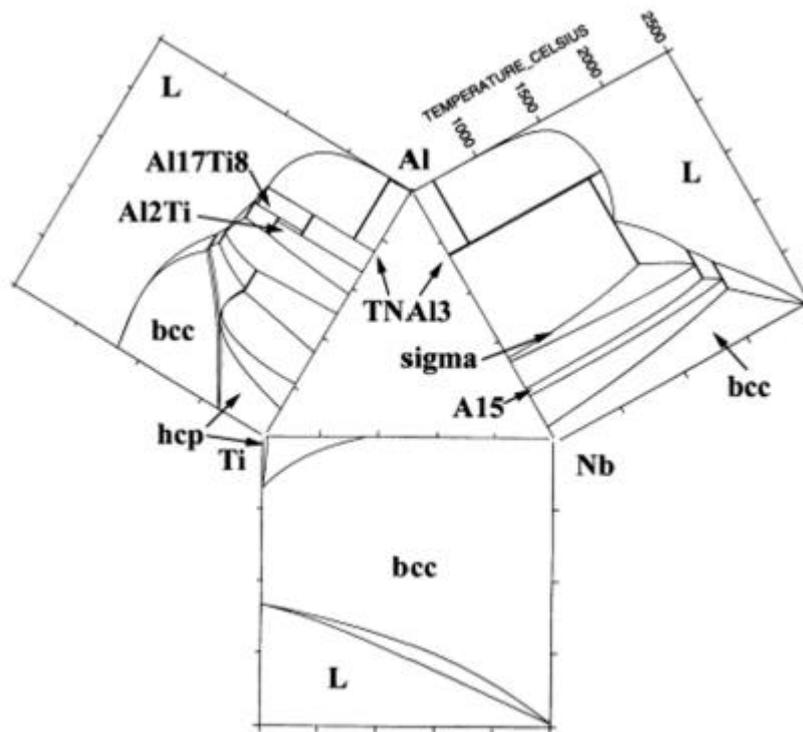


Figure 6: Calculated binary phase diagram components of the Nb-Ti-Al system. The liquid phase is designated by L.

The Phase Fraction versus temperature curve does not show the composition of the phases at equilibrium. However since this data is calculated at each temperature it can be readily displayed as illustrated below. Moreover, it should be evident that this representation can be readily applied to multicomponent alloy with four or more components to describe materials used in commercial practice⁹⁻¹⁴. This is illustrated below for a quaternary Nb-Ti-Cr-Al alloy.

However, before turning to this alloy it is instructive to consider the case of ternary isopleths which are useful in considering alloys for applications in coating, joining and manufacture of composite structures. Figures 10 and 11 are isopleths in ternary subsystems of Nb-Ti-Cr-Al. The first is along the join from Cr to 66.7atom%Ti - 33.3atom%Nb, a composition that corresponds to an alloy used for superconducting wire². The isopleth can be sketched by connecting the Cr apex of the triangles in Figure 3 with a point on the Ti-Nb base that is 1/3 the way from Ti to Nb at each temperature. Figure 10 shows the computer-generated results, which are quite simple because the ternary is simple.

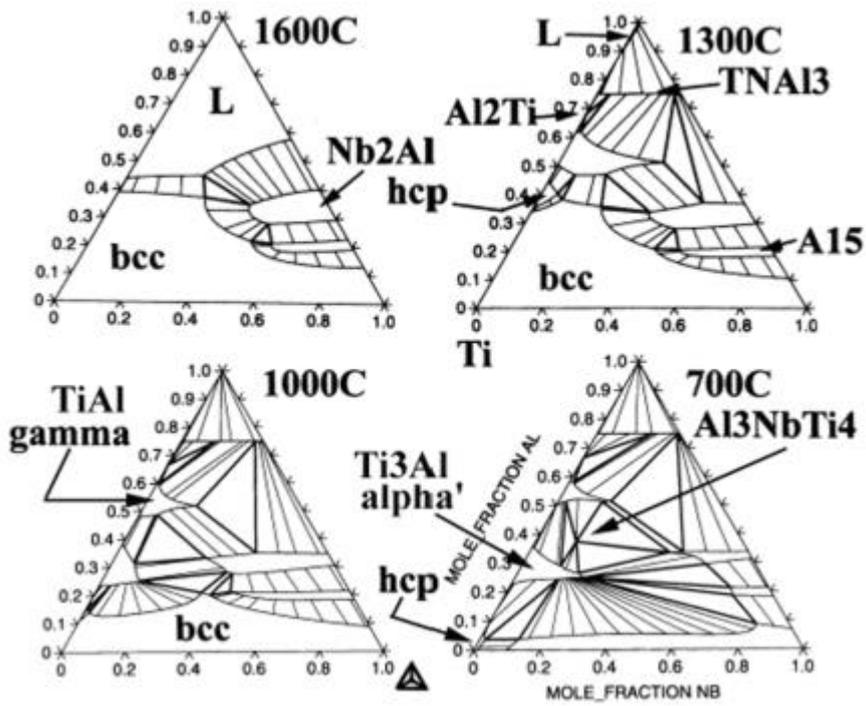


Figure 7: Calculated isothermal sections in Nb-Ti-Al at 1600, 1300, 1000 and 700°C. Two-phase regions are identified by tie-lines, three-phase regions by triangles and single-phase regions are labeled.

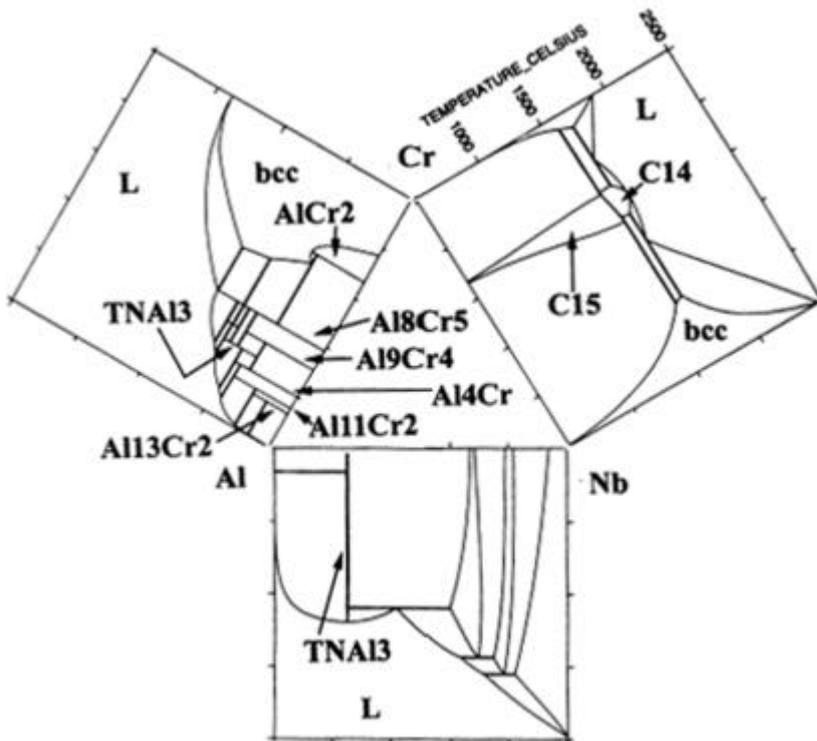


Figure 8: Calculated phase diagram components of the Nb-Al-Cr system. The liquid phase is designated L.

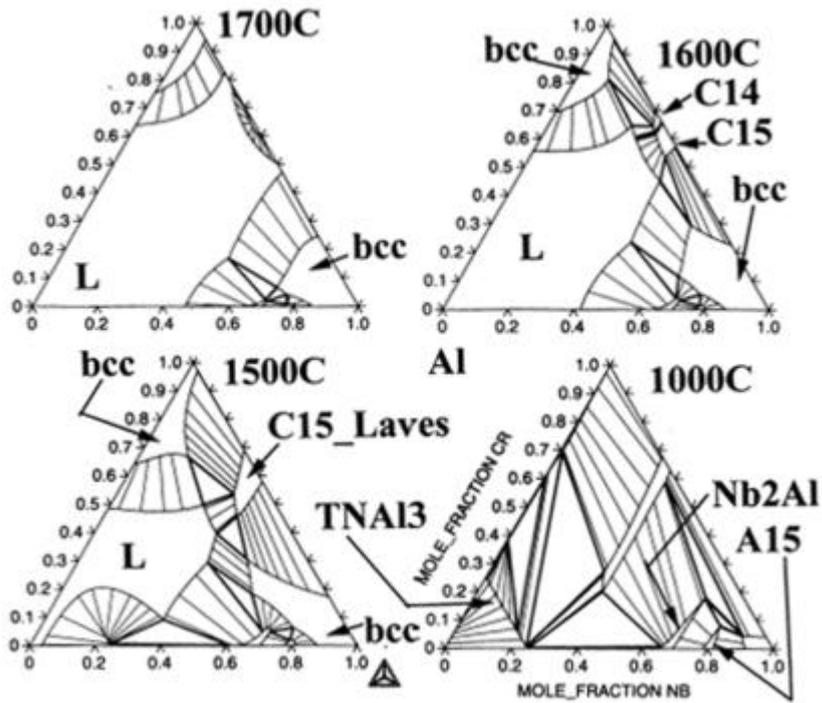


Figure 9: Calculated isothermal sections in Nb-Al-Cr at 1700, 1600, 1500 and 1000°C. Two-phase regions are identified by tie-lines, three-phase regions by triangles and single-phase regions are labeled.

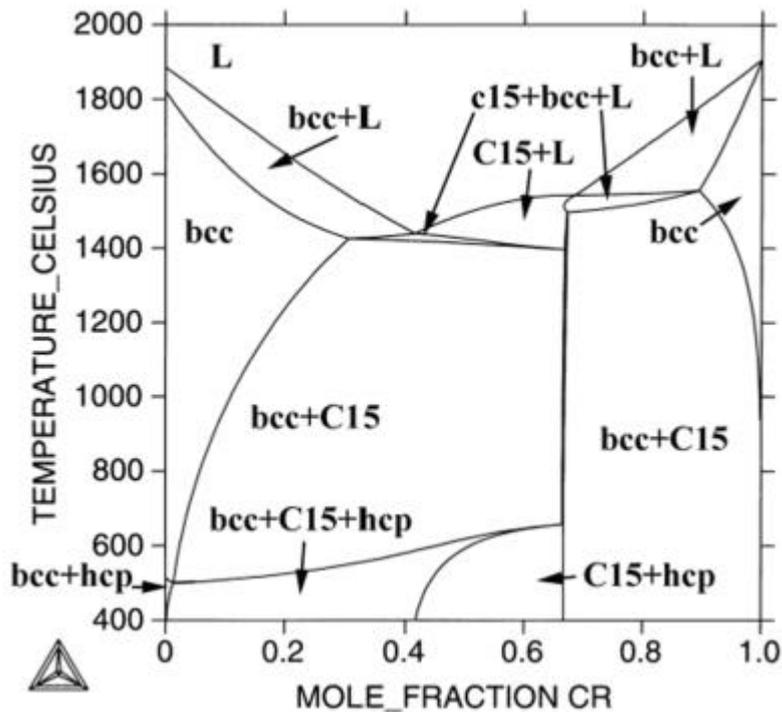


Figure 10: Calculated isopleth along the join from Cr to Ti-33atomic%Nb (see figures 1 and 2). Note that the tie-lines need not lie in plane of the isopleth.

As the caption indicates the Tie-Lines need not lie in the plane so that compositions cannot be read from this figure except in the single phase fields. Figure 11 shows a much more complex isopleth in the Al-Ti-Cr system along the join from Al to Ti-50atom%Cr. The complexity can be readily anticipated by the simple construction previously described.

Figure 12 is the phase fraction versus temperature curve calculated for a Nb-21.2wt%Ti-7wt%-1.8wt%Al alloy. Equilibrium solidification begins at about 1975C and ends at about 1750C. On further cooling a bcc phase that forms from the melt is the only stable phase until the C15 Laves phase begins to form below 1100C. Subsequently the Ti₃Al(alpha') and hcp phases precipitate from the bcc phase as the temperature is decreased. In the temperature range between 1100C and 1750C the alloy is single phase bcc with the same composition as the liquid however the subsequent precipitates contain Nb and Cr(C15), Ti and Al(alpha') and Ti(hcp). This description provides a concise and complete picture of the phase stability of this alloy as a function of temperature.

In order to obtain a broader view, the isopleth in Figure 13 can be generated fixing the ratio of Al to Cr and Cr to Ti and varying the Ti and Nb over the entire range. The isopleth locates the 70wt%Nb alloy, which corresponds to that in Figure 12. Comparison of the transition temperatures for this alloy with those in Figure 12 shows that they are in good accord. Figure 14 displays the composition of the bcc as a function of temperature as it experiences the phase changes on cooling (or heating) in Figure 12 or 13. Between 1100 and 1750 the single phase bcc exhibits the starting composition of the alloy. Below this temperature the sequential precipitation of the C15, alpha' and hcp phases results in the alteration of the composition of the bcc phase. Also it is possible to display similar temperature dependent curves for the composition of each of the abovementioned phases.

Finally phase fraction versus temperature curves can be run for any niobium concentration along the abscissa in Figure 13 from near zero to nearly pure Nb. The corresponding composition versus temperature curves can also be generated. As indicated above, the concentration can be read or inferred only for the single phase bcc and liquid phase regions. However the compositions of the coexisting phases in the multi-phase regions can be retrieved and displayed as in Figure 14. Figures 15 and 16 show a Scheil simulation of the freezing of the Nb alloy as compared with equilibrium cooling. This simulation consists of making 1C steps below the 1975C temperature where the bcc starts to form, separating the bcc phase and repeating the 1C cooling step. Figure 16 follows the composition of the bcc phase. Two features are immediately evident. First, the liquid phase is present in the Scheil simulation process to a much lower temperature than under equilibrium cooling conditions. Second, substantial segregation of Nb, Ti and Cr is predicted by the Scheil freezing model.

A more detailed model calculation of this process can be employed which considers diffusion in the liquid and solid phases. This calculation generally leads to results midway between the two curves in Figure 15.

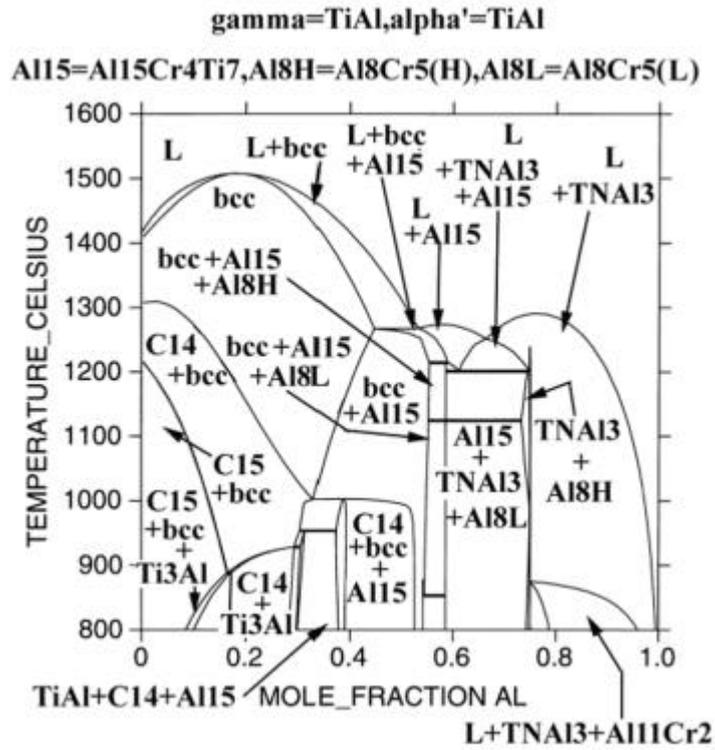


Figure 11: Calculated isopleth along the join from Al to Ti-50atomic%Cr (see figures 3 and 4). Note that the tie-lines need not lie in plane of the isopleth.

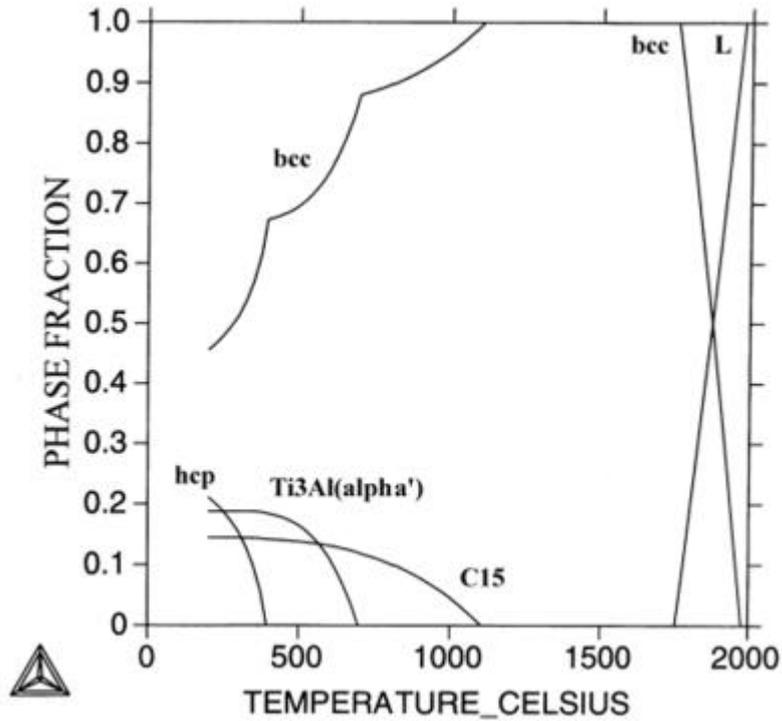


Figure 12: Calculated phase fraction vs. temperature curve for a Nb-21.2weight%Ti-7weight%Cr-1.8weight%Al alloy.

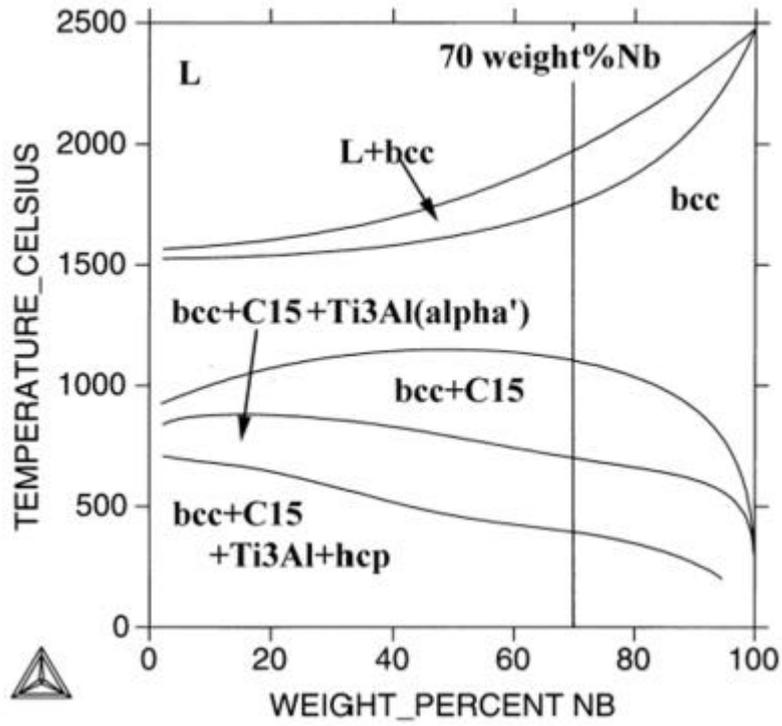


Figure 13: Calculated isopleth constrained by the conditions that weight%Cr = 4weight%Al and weight%Ti = 3weight%Cr.

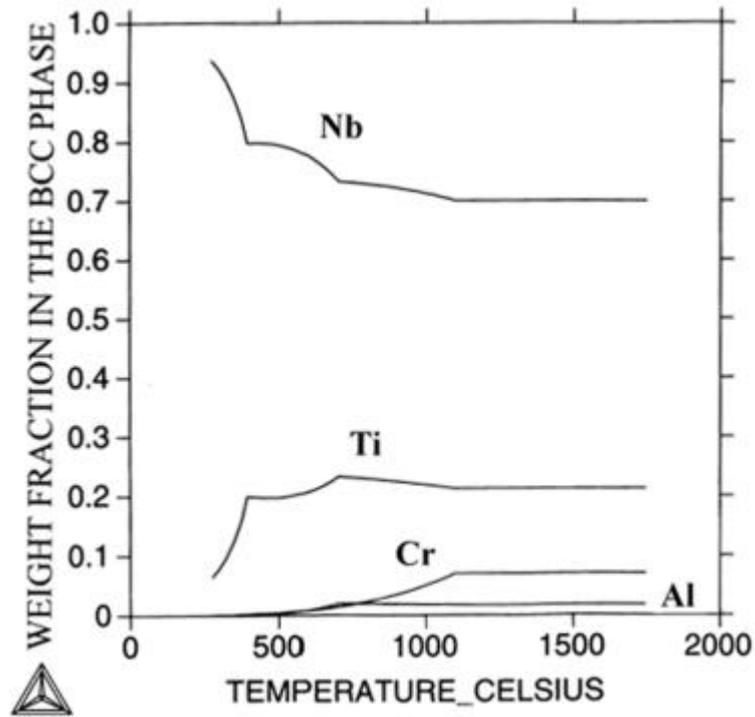


Figure 14: Calculated composition of bcc phase of the niobium alloy displayed in figures 12 and 13 as a function of temperature.

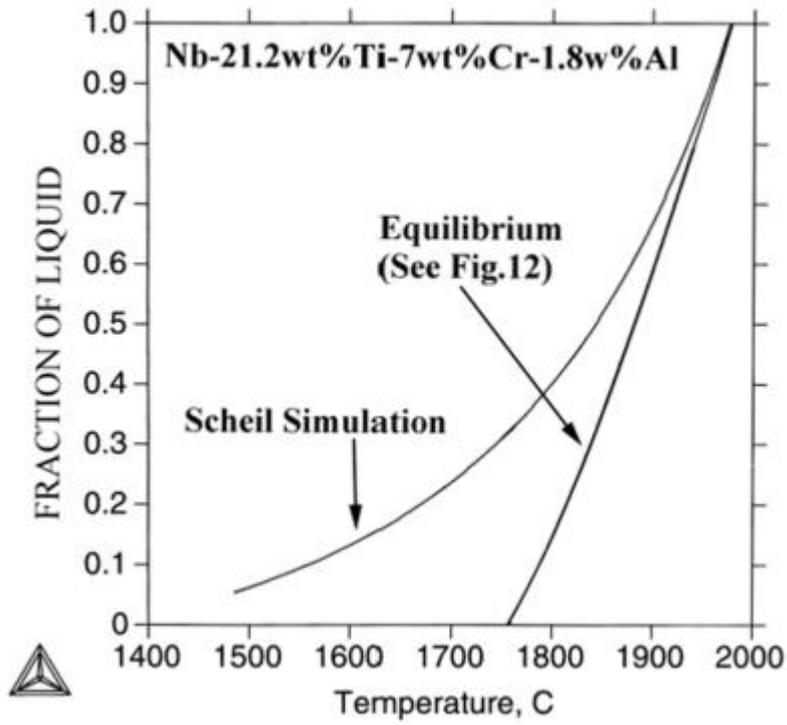


Figure 15: Comparison of equilibrium freezing and Scheil simulation results calculated for a Nb-21.2weight%Ti-7weight%Cr-1.2weight%Al alloy.

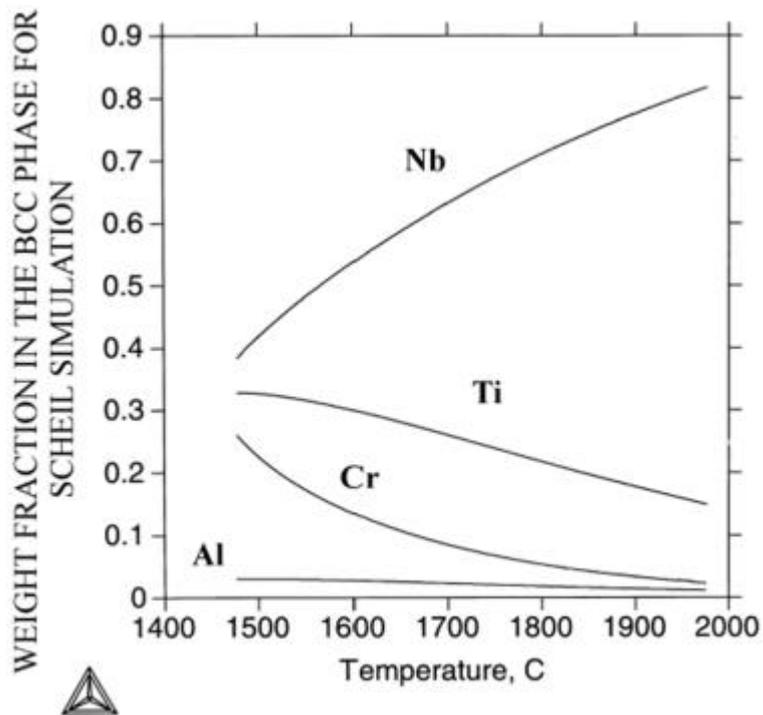


Figure 16: Calculated composition of bcc phase in Scheil simulation freezing of a Nb-21.2weight%Ti-7weight%Cr-1.8weight%Al alloy.

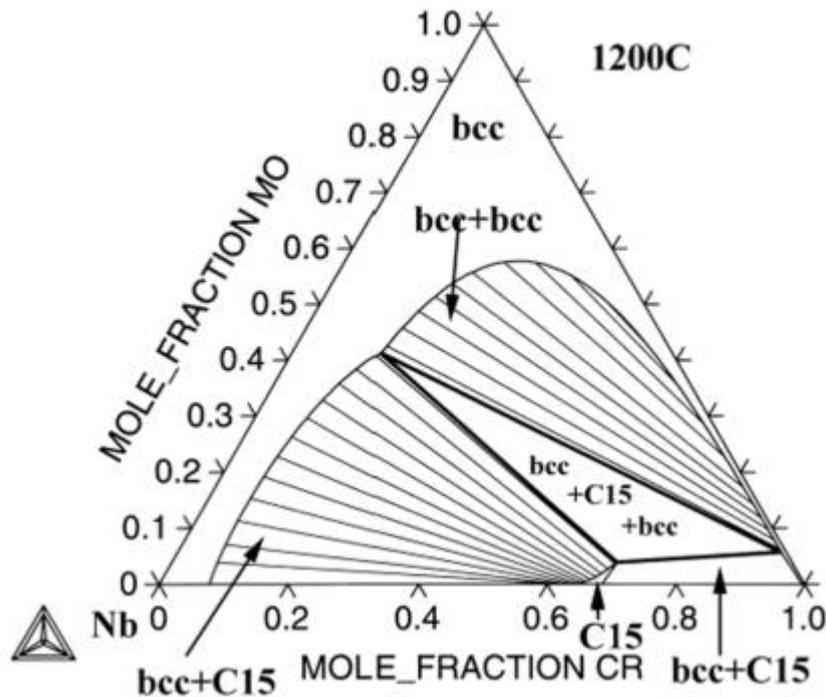


Figure 17: Calculated isothermal section in the Nb-Cr-Mo system at 1200°C.

Summary

The calculations of the Nb-Al-Cr-Ti system presented above illustrate the advantages afforded by a coupled thermochemical/phase diagram description (CALPHAD) of Nb alloys. In the earlier 1981 Nb Symposium¹⁻⁴ reference is made to 23 elements that are alloying additions or significant impurities in Nb alloys used in a variety of applications. In addition to Ti and Cr there are 11 additional transition metals, five other metals, Cu, Al, Cd, Sn and Pb and five interstitial elements (H, B, C, N, O). Contemplating creation of a 24 (include Nb) element database seems like an awesome task. However the database could be split up into various segments by application or categories (i.e. hardmetals, steels, superalloys, superconductors, etc.) and it would be apparent that existent databases would cover a good part of the requirements or need only minimal improvement to be sufficient. At the 1981 Symposium there was no mention of calculated phase diagrams as CALPHAD was a new journal (volume 1, 1977). However it should be noted that Argent¹, p326, makes mention of the fact that “occasionally a miscibility gap develops in an unexpected way” in the bcc Nb-Cr-Mo phase at 1200C. In fact Argent was not aware of the calculated bcc miscibility gap in Cr-Mo with a maximum at 941C, which would lead one to expect that a bcc miscibility gap would appear in Nb-Cr-Mo at 1200C. Indeed Figure 17 provides a current calculation of the 1200C isotherm that shows such a miscibility gap. It is quite likely that at the next niobium symposium there will be many examples of useful applications of CALPHAD analyses of Nb alloy systems.

Acknowledgement

This paper is dedicated to the memory of my dear friend and colleague of 30 years Dr. Himo Ansara who died suddenly on 25 March 2001. Himo was a founding member of CALPHAD and a pioneering worker in the development of this new field of prediction of phase diagrams of

multicomponent systems based on thermochemical data and models for condensed phases. It will be many years before all of his contributions to this field will be understood. He will be sorely missed.

References

- (1) B.B.Argent, "Phase Diagrams of Alloys Based on Niobium"Niobium, Proceedings of the International Symposium, H.Stuart,ed.TMS,Warrendale,Pa(1981)325.
- (2) W.K.McDonald,"Fabrication of Niobium and Niobium Alloys",ibid 225.
- (3) C.English, "Physical,Mechanical and Irradiation Behavior of Niobium and Niobium-Base Alloys"ibid 239.
- (4) Y.Furato, "Fundamentals of Niobium Based Superconductors"ibid 445.
- (5) .T.B.Massalski,Ed.Binary Alloy Phase Diagrams (Metals Park,OH:American Society for Metals,1996).
- (6) P.Villars,A.Prince and H.Okamoto,eds.Handbook of Ternary Alloy Phase Diagrams vols1-10 (Metals Park,OH:American Society for Metals,1995).
- (7) Cumulative Index,J.Phase Equilibrium,18(1997)677.
- (8) L.Kaufman and H.Bernstein "Computer Calculation of Phase Diagrams" Academic Press,N.Y.,N.Y.
- (9) N.Saunders and A.P.Miodownik, "CALPHAD" Elsevier Science Ltd (1998).
- (10) L.Kaufman,"Computational Thermodynamics and Materials Design"(Paper presented at the 130th Annual Meeting of TMS,New Orleans,LA Feb.2001,J.Metals,52(2000)8 to be published in CALPHAD 25(2001).
- (11) M.S.Gagliano and M.Fine "Precipitation Kinetics of Niobium Carbide and Copper in a Low Carbon,Chromium-Free Steel" ibid 132.
- (12) L.Kaufman,J.Phase Equilibrium,14(1993)413.
- (13) P.J.Spencer,MRS Bulletin,April 24(1999)18.
- (14) B.Sundman and J.Agren,MRS Bull.April(1999)pp32(P.J.Spencer,Ed.p18).
- (15) C.Servant and I.Ansara,Ber.Busenges.Phys.Chem.102(1998)1189.
- (16) I.Ansara,TC-Ni-Database in Thermo-Calc VerN 2000.
- (17) N.Saunders in G.Shao and P.Tsakiropoulos,Intermetallics,7(1999)579.
- (18) T.J.Jewett and M.Dahms,Z.Metallkd.87(1996)254.
- (19) C.R.Hunt and A.Raman,Z.Metallkd.59(1968)701.

(20) L.Kaufman and H.Nesor.CALPHAD,2(1978)78.