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Exploration of Multicomponent Phase Diagrams and Evaluation of Calphad Databases

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Abstract: **With the emergence of modern materials such as high-entropy alloys (HEAs) and the ever-increasing demand for improvement in conventional metallic materials, it becomes essential to have multicomponent phase diagrams. The availability of such diagrams, however, is very scarce. Calphad (CALculation of PHAse Diagram) method offers a way to construct such diagrams, combining theoretical and experimental methods into appropriate computational programs. The various visualization of multicomponent diagrams, the associated advantages and compromises are reviewed in the present work with a few example calculations on CoCrFeNi and AlCoCrFeNi systems. Besides, the accuracy of the Calphad method relies mainly on the available multi-component thermodynamic databases. A few of such databases are evaluated in this work as well.**

Index Terms: **Phase diagrams, Calphad, Gibbs energy, Thermo-calc.**

I. Introduction

Research groups of Yeh and Cantor independently came up with the earliest works on HEAs [1], [2]. These alloys have recently attracted significant academic interest [3]. HEAs have a stark difference from conventional alloys in terms of composition. Conventional alloys have one major element called the base element, e.g. Fe is the base element in steel. On the other hand, HEAs have multiple principal elements, often five or more, and no single element can be called as base element [4], e.g. equiatomic CoCrFeMnNi. When such a composition occurs as a solid solution, it will have high configurational entropy. This thermodynamic factor depends on the number of elements used and not on the type of elements used. Yeh et al. [1] proposed that the high entropy may dominate the competition among various thermodynamic factors of competing phases and improve the stability of the simple solid solution over other phases. The reality, however, turned out to be more complex. Microstructures of HEAs have been observed to be heavily depending on the type of elements used. From a simple single-phase solid solution to complex multi-phase microstructures were reported in various HEAs [5]. The field, however, has opened large unexplored metallic materials for investigation.

Since possible number of HEAs are astronomically high, compositional design is a necessary step in HEA research, which involves finding useful compositions to achieve a suitable microstructure vis-à-vis properties. Investigating the multicomponent phase diagrams for HEAs is the most important activity since phase diagrams are the roadmaps for compositional design. This activity greatly reduces the experimental effort to a small set of alloys rather than doing trial and error, which requires monumental efforts due to the shear immensity of possible alloy compositions. In this regard, the biggest challenge is that multi-component phase diagrams are almost unavailable beyond ternaries and experimentally determining such phase diagrams is also extremely difficult.

The Possible number of HEAs are astronomically high. A necessary step in HEA research is to find useful compositions to achieve a suitable microstructure vis-à-vis properties. Phase diagrams are the roadmaps for composition selection. Multi-component phase diagrams are almost unavailable beyond ternaries and experimentally determining such phase diagrams is also extremely difficult.

There are simple empirical rules which are fast and quite useful to predict the likely microstructure. These rules are not very sophisticated, e.g. one alloy is predicted to have one microstructure at all temperatures. Besides, significant exceptions are reported for such rules [5]. However, none of these methods are as sophisticated as using a phase diagram for compositional design.

Apart from these simple methods, the Calphad method is robust, as it gives the phase diagram directly. The drawback is that the method requires reliable multicomponent Gibbs energy databases [6]. One reason for discrepancies is, the unavailable or inaccurate Gibbs energy databases. With such databases, the rapid screening methods for useful HEA compositions face serious accuracy issues [7].

One of the reasons is that only unary, binary and ternary Gibbs energy descriptions are usually developed and used. Data for higher order systems are obtained using extrapolation from lower order systems. In order to account for the higher-order effects, correction terms are required. Beyond ternary effects, usually, the contribution of higher order effects diminish and are usually ignored [8], which can

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cause significant issues in certain alloys. Further, developers focus on designing the Gibbs energy databases, usually, to work for specific compositional ranges. Evaluating the uncertainties associated with using the databases beyond such ranges is necessary for efficient alloy discovery.

Therefore, evaluation of the available databases is important which is attempted in the present work. However, firstly, the visualization of multicomponent phase diagrams is difficult since often it is a 2 dimensional representation. Therefore, various ways of looking at such a multicomponent composition way need to be explored. A few standard ways are revised in the present work with a few example calculations, outlining the advantages, calculation methods and compromises.

II. Modelling & Simulation Methods:

Thermo-Calc software were used for calculations. TCNI and SSOL thermodynamic databases were used in Thermo-Calc software. The databases contain Gibbs energy descriptions for the phases that are competing for stability. These descriptions are obtained through statistical curve fitting procedures, to obtain model parameters of Gibbs energy. The models are fitted to various kinds of experimental and theoretical data that are in some way related to Gibbs energy. The descriptions are compiled into databases, addressing various compatibility and higher order model parameters. For construction of isoplethal section, for example, in a four component system, the ratio between the mole fractions of three of the elements is maintained constant, as the mole fraction of the fourth element varies in x axis and temperature in y axis. For the construction of phase fraction plots, the composition is fixed at one value and the temperature is varied. It is also called as one axis diagram since only one variable is changed. The equilibrium phases are predicted in all these diagrams through the process of Gibbs energy minimization. Mathematically, it is a constrained optimization technique, where the constraints are compositions and temperature. The pressure is not varied and is kept equal to atmospheric pressure.

III. Visualizations Of Multicomponent Phase Space

Reported Calphad studies use various visualizations of phase diagrams in multicomponent space. One type is an isoplethal section, where restrictions on composition are used as conditions. Such diagrams are similar to conventional binary phase diagrams in terms of axes (T vs x) [9]–[12]. Such diagrams are made in the present study as well. Quaternary diagrams at a single temperature using a tetrahedron are reported [13]. A stack of pseudo quaternary diagrams was proposed to represent the quinary diagram. A 3D compromise representation of a 4D polytope using an isometric projection was also reported to visualize quinary diagram, preserving many details. Representations using graph theory were reported to have severe compromises [5]. Recently, parallel coordinate plots [14] were applied to HEAs [15], [16], which represent compositional relationships of phases at a single temperature. When it comes to fixed compositions, the widely considered representation is a phase fraction plot, which is made in the present study as well. In phase fraction plot, the amount of equilibrium phases is plotted against temperature [17]–[20].

IV. Results and Discussion

Isoplethal section or vertical sections or pseudo binary sections of multicomponent Co-Cr-Fe-Ni alloys are shown in Fig. 1 a-d. The Co, Cr, Fe and Ni elemental mole fractions were varied respectively. The way to visualize the diagrams, for example, Fig. 1a, is that at the left end of x axis the phases present in CrFeNi equiatomic ternary alloy are shown. As the Co content increases in the x axis, let's say to a value of 0.2, the other elements Cr, Fe and Ni maintain their equiatomic ration and occupy a cumulative mole fraction of 1 - 0.2 = 0.8. The right end of the diagram shows the phases in pure Co. Similarly, the diagrams in Fig.1 b-d can be visualized. In such diagrams mole fractions of all the four elements change in x axis. Apart from such an x axis, one can keep the mole fraction of two elements constant and allow that of the other two elements vary. Similar to Fig. 1, one can understand the five component diagrams shown in Fig. 2a and b for Al-Co-Cr-Fe-Ni alloys.

Although such diagrams are quite useful in giving familiar visualization of a phase diagram, we can sense that these diagrams show only a tiny portion of the four component phase space, i.e., these are merely four 2-dimensional slices of such a vast space. Thus, a severe compromise is present here in not showing potential compositions with combination of phases suitable for a particular application.

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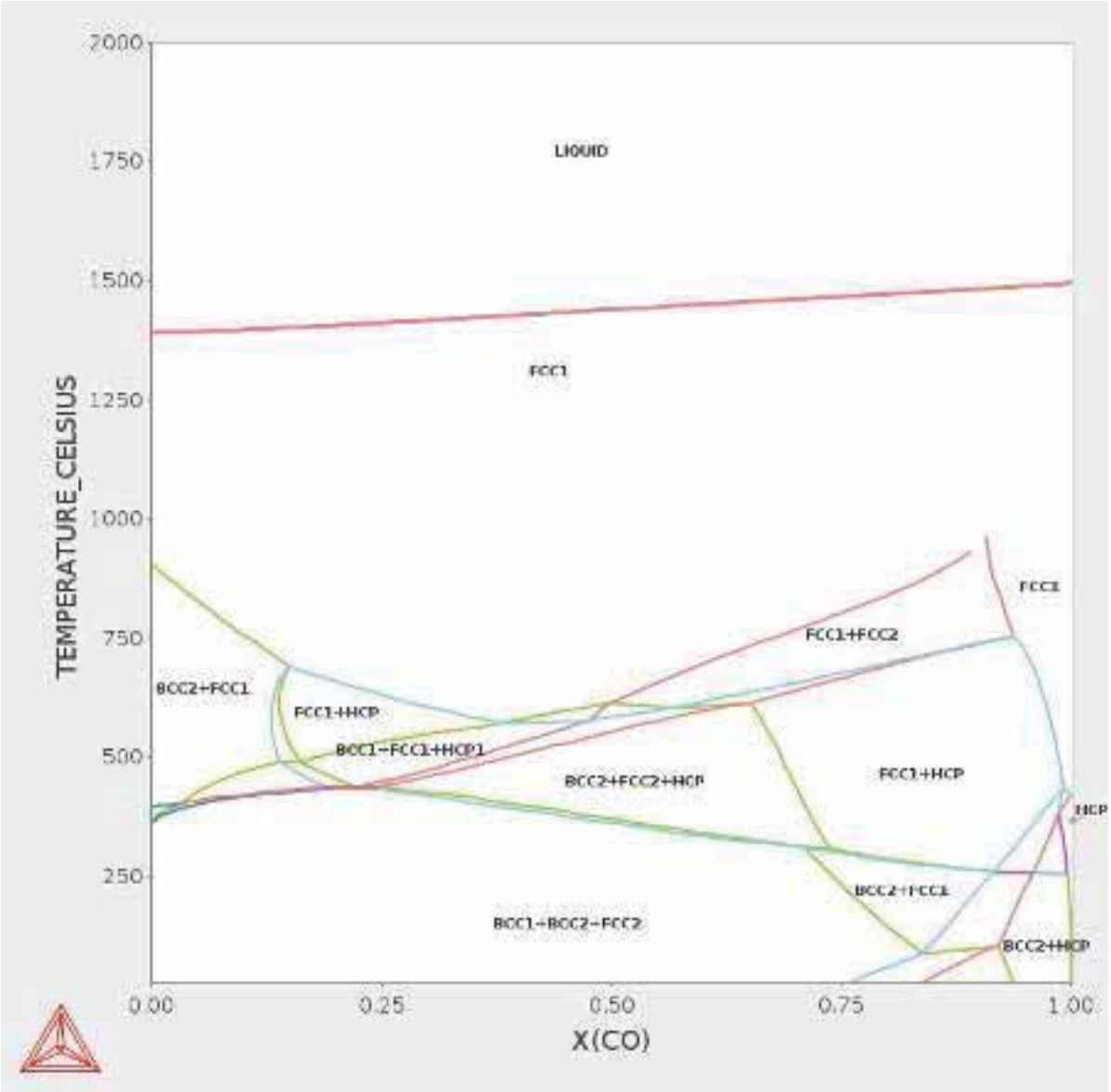

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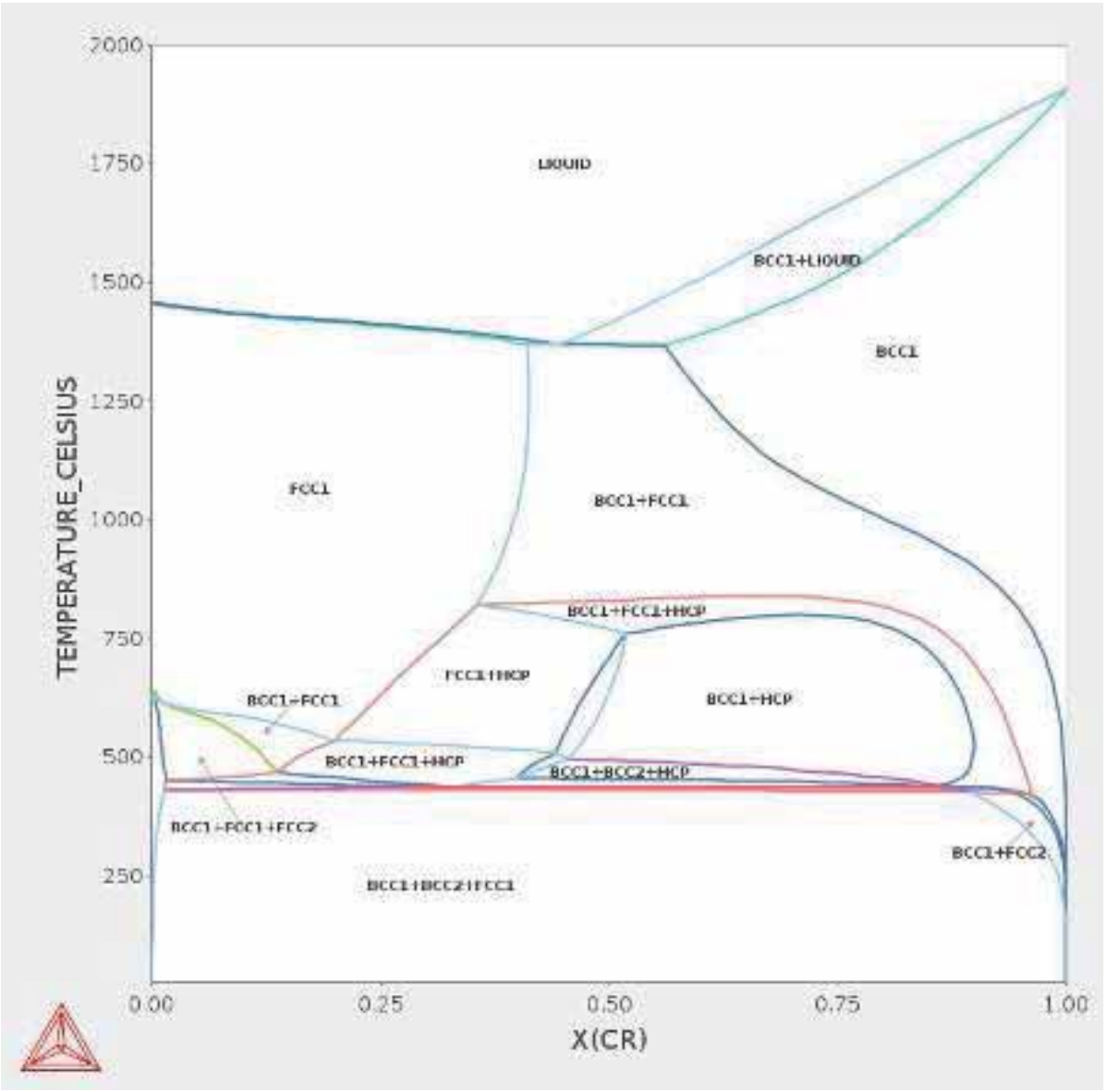

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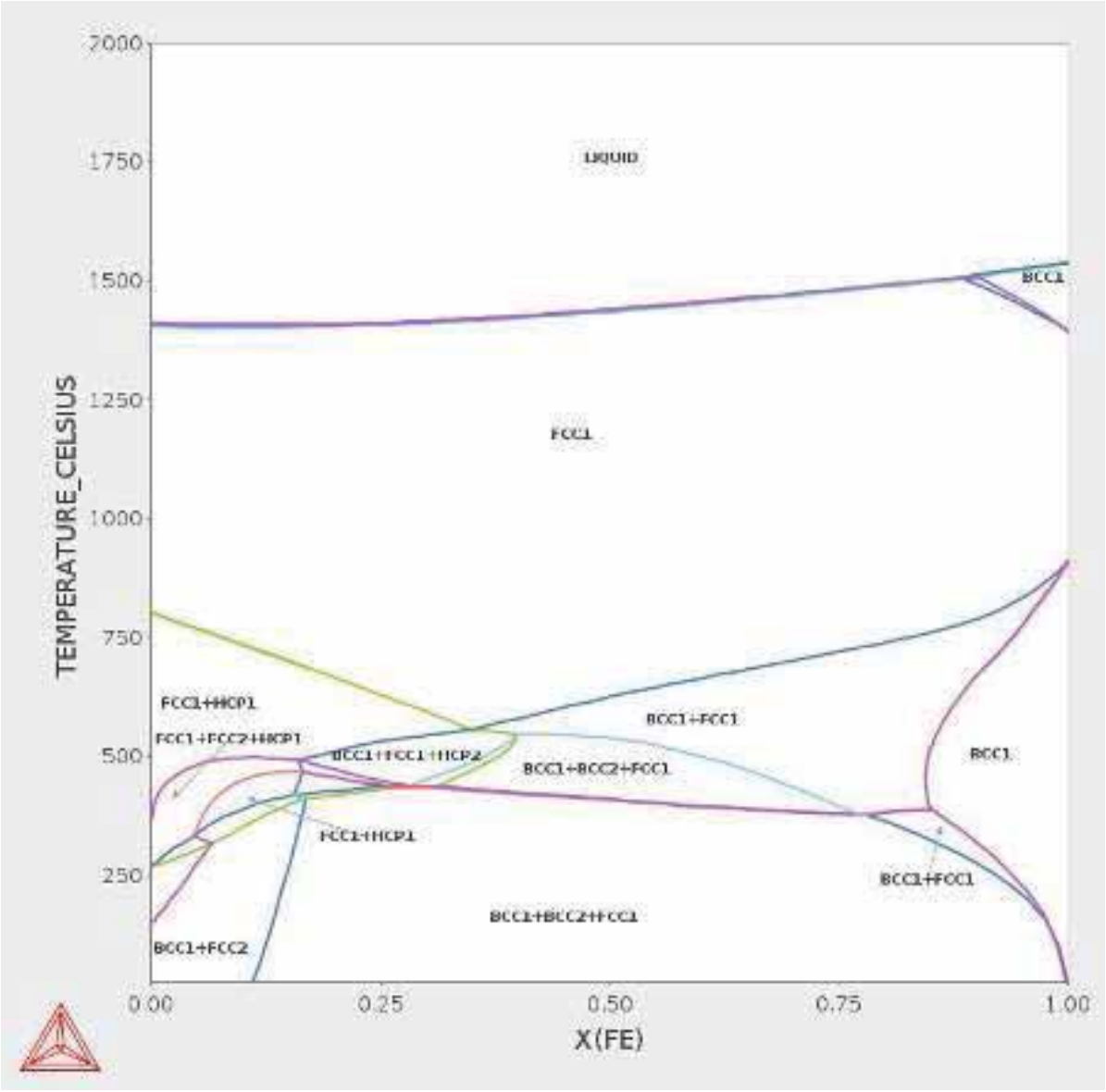
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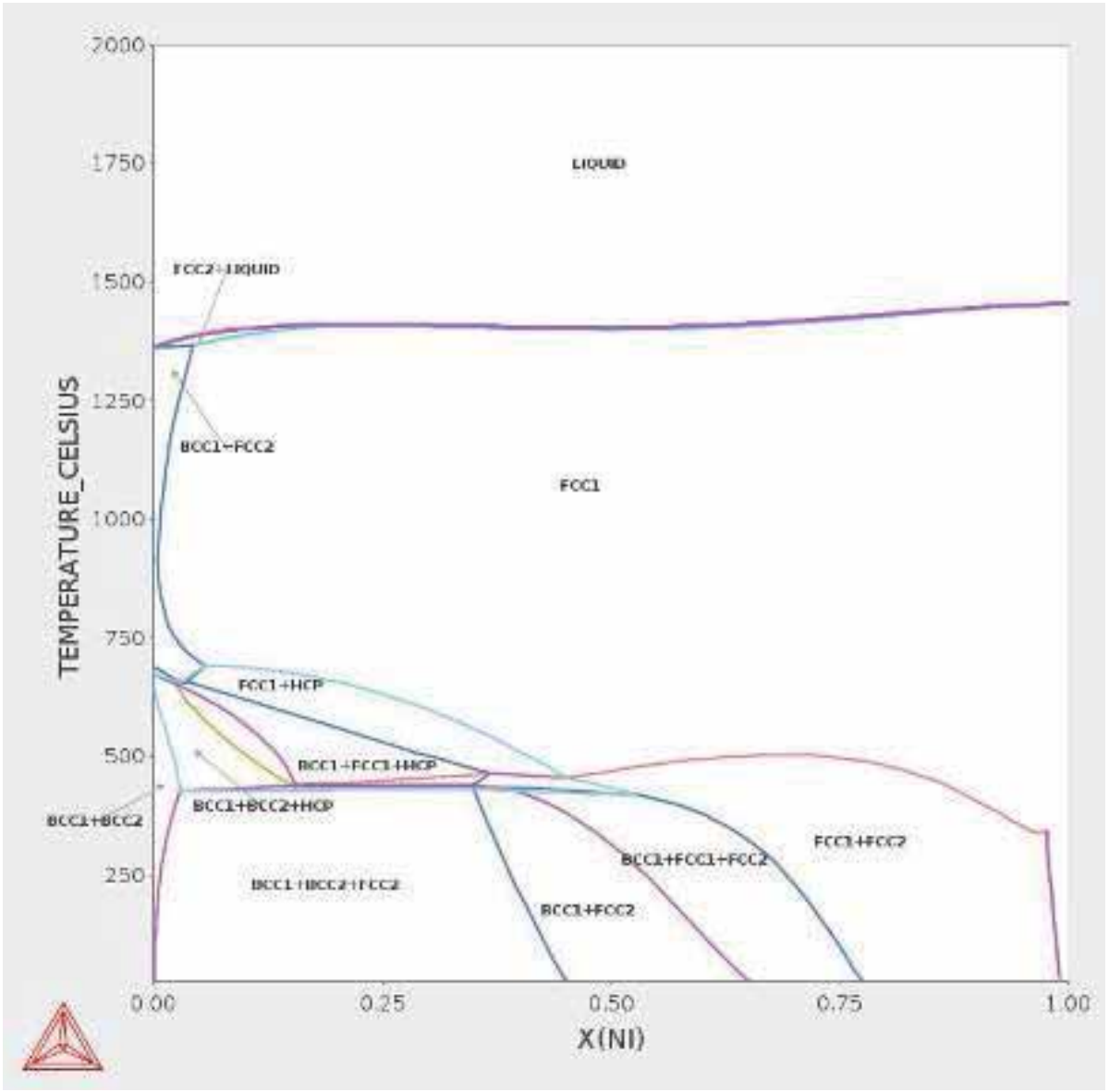
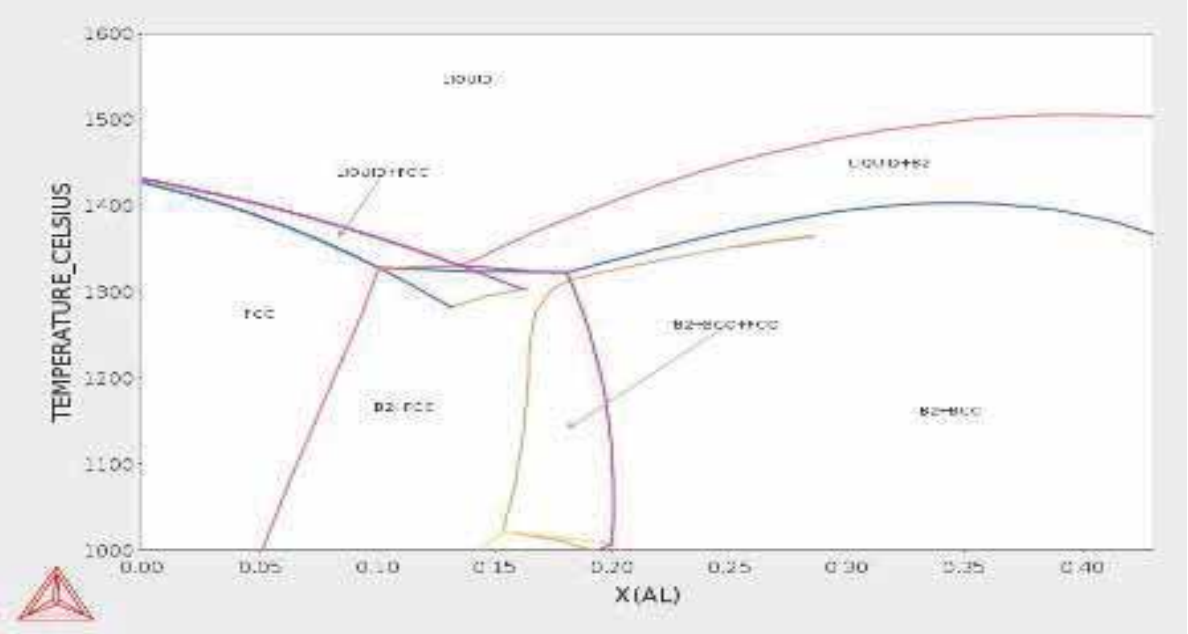


(d)

Figure 1. Co-Cr-Fe-Ni isoplethal sections with varying amounts of a) Co, b) Cr, c) Fe and d) Ni in x axis.



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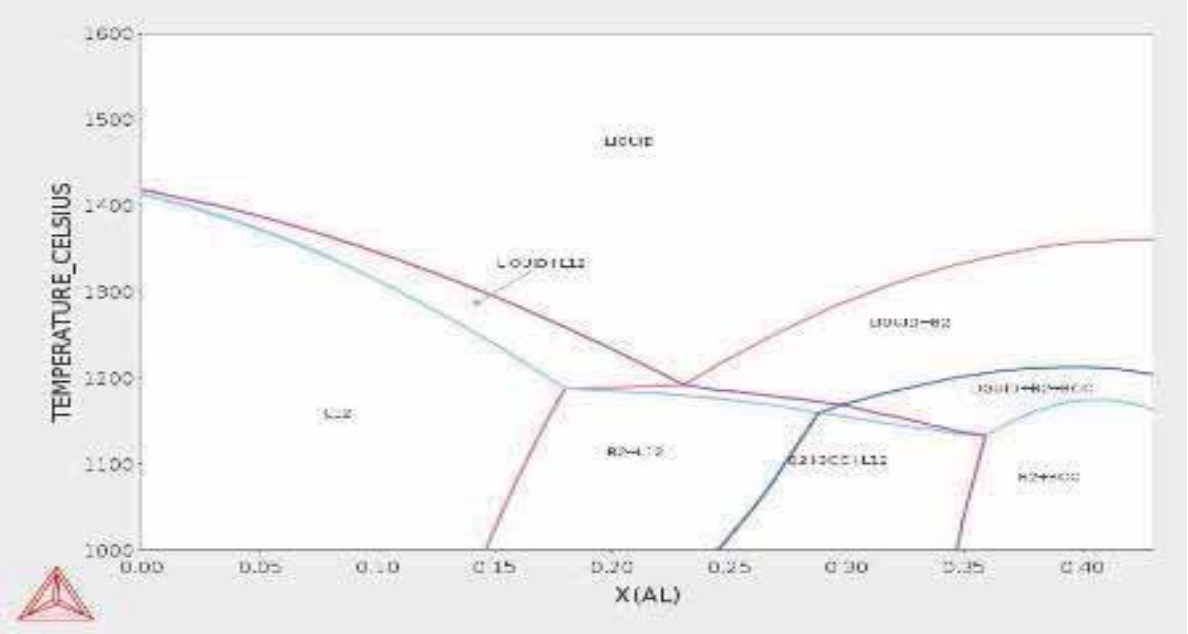
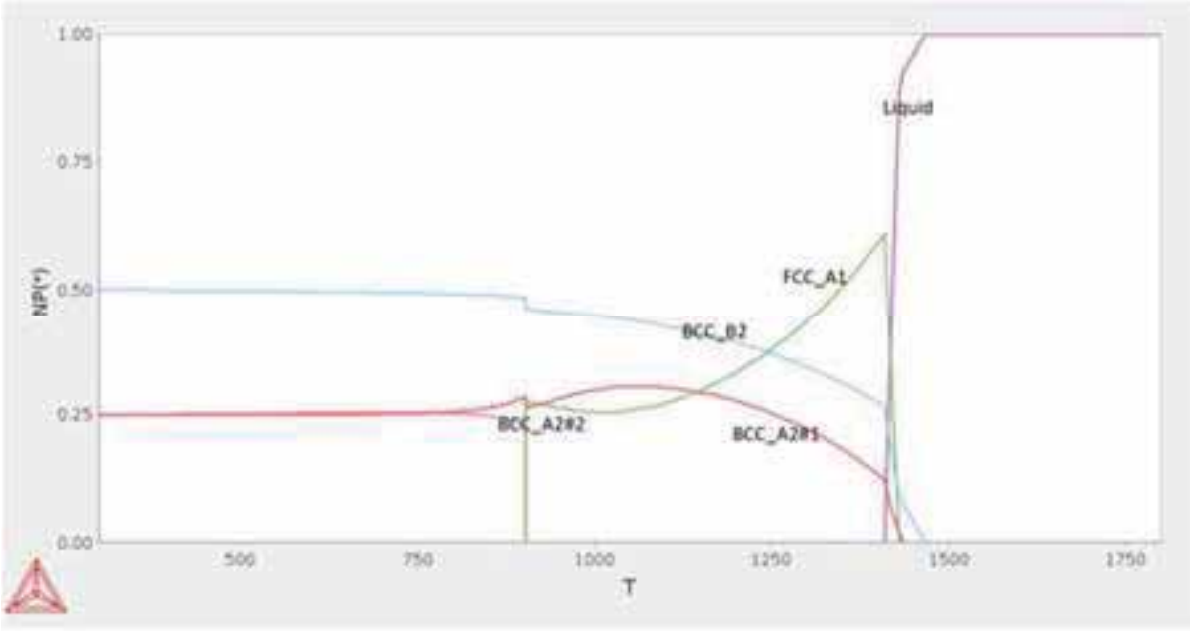


(b)

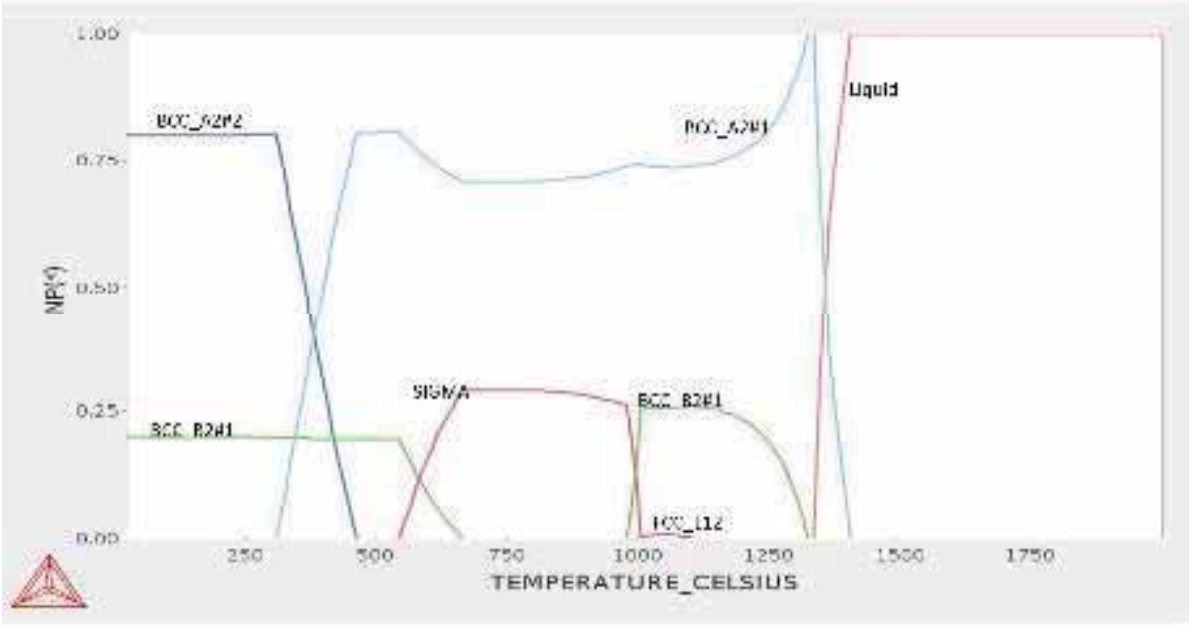
Figure 2. Al-Co-Cr-Fe-Ni isoplethal sections plotted using the data bases a) TCNI and b) SSOL with variation of Al mole fraction in x axis.

In Fig.2, a comparison between two different databases are made, TCNI and SSOL. When the experimental results reported in literature [3] are compared with these diagrams, the melting points, primary solidifying phases, etc. match reasonably well with the Fig. 2a compared to Fig. 2b. The prime reason for such a difference is mainly due to the included assessed data of binary and ternary subsytems in each database. In Al-Co-Cr-Fe-Ni system, there are 10 binary and 10 ternary subsystems. Both the databases have all the ten binary subsystems included. When it comes to ternary SSOL5 hardly has data for only one system whereas TCNI has data for about 7 systems. Therefore, the better accuracy is achieved with TCNI database.

Phase fraction plots or the one axis diagrams are given in Fig.3a and b for the single fixed composition of AlCoCrFeNi equiatomic alloy. The advantage in such diagrams is that the phase fraction information can be directly obtained whereas, in a conventional T-x diagram, it has to be calculated by applying lever rule separately at each temperature. The compromise however is, phases at any other composition cannot be seen.



(a)



(b)

Figure 3. a) AlCoCrFeNi phase fraction plots drawn using the databases a) SSOL b) TCNI. (NP- Mole fraction of phases).

Again, severe differences are seen and the TCNI database gives better results compared to reported experimental data in terms of melting point and primary solidifying phases. However, when it comes to solid state, the FCC_A1 phase is experimentally observed at a higher fraction compared to what is predicted using TCNI. The SSOL database on the other hand, shows the FCC phase content to be higher, matching closely with the experiment. However, with SSOL

database, FCC appears as a primary solidifying phase which is not matching with the experimental reports.

Another aspect of difference is the appearance of sigma phase. It is experimentally reported to appear at intermediate temperatures, which is predicted using TCNI database. However, the exact range of its stability and the phase content have certain inaccuracies [21]. SSOL database was not capable to predict the sigma phase since the solution phases are given focus in it on top of missing ternary data.

V. Conclusions

Isoplethal or vertical or pseudo binary sections for Co-Cr-Fe-Ni and Al-Co-Cr-Fe-Ni systems are calculated. Such diagrams are a useful way to visualize the multicomponent phase space, although there are compromises since these are only 2-dimensional slices thus, such a vast phase space. One axis or phase fraction plots are useful in obtaining equilibrium phase fraction data along with the stable phases for a fixed multicomponent compositions.

The evaluation of Calphad databases SSOL and TCNI are made. TCNI calculations are, in general, better than SSOL. The reason is found to be mainly the included number of ternary descriptions. TCNI has 7 ternary systems of Al-Co-Cr-Fe-Ni system, whereas the SSOL has only one.

When it comes to predicting topologically close packed phases such as σ-phase, TCNI is better, although the stability range and the phase fraction have significant inaccuracies compared to experiments. There is a scope to improve such databases with more ternary data and possibly higher order data, Revisiting models may be one of the ways to improve the databases, however, in the present work it was not explored.

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