Analysis of the phase equilibria in multicomponent systems using graphs

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The possibility of polyhedration of multicomponent systems by the graph method was demonstrated using the Ni–V–Cr–Mo–Re system as an example.

Phase diagrams form the basis for the majority of studies in the solid-state chemistry and materials science. However, promising multicomponent ($n > 4$) phase diagrams are presently difficult to study and very labour intensive. It is reasonable to subdivide this problem into two parts. Firstly, all phases formed in the test system and the phase equilibria are determined. This procedure is called the polyhedration of the system. Next, a portion of the system is examined in detail. This portion that shows promise for the development of new materials is chosen on the basis of data obtained at the first stage. Thus, the number of required experiments is considerably decreased.
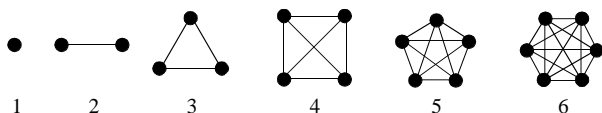

Figure 1 Multiphase equilibria represented as graphs.

The graph method[1–3] is holds the greatest promise for formalisation, systematisation, analysis and prediction of the structure of multicomponent systems. Essentially, this method consists in that any *N*-phase equilibrium can be represented as a complete graph with *N* vertices (Figure 1). In this case, each phase is depicted as a node of the graph (a point regardless of the number of components), and the edges represent the existing equilibria between the two corresponding phases. The graph that includes all equilibria in the system at specified temperature
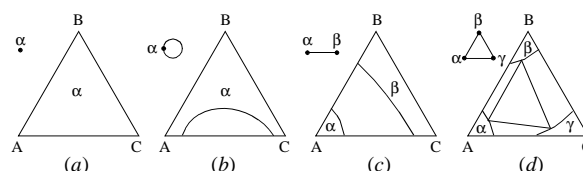

Figure 2 The simplest isothermal cross-sections of ternary systems represented as graphs.

and pressure is a formalised isothermal cross-section of the phase diagram.

The polyhedration of an *n*-component phase diagram by the graph method can be performed using data on the phase equilibria in $(n - 1)$-component systems in the following three consecutive stages:

(1) Presentation of the isothermal cross-sections of $(n - 1)$-component systems as graphs. As an example, Figure 2 shows the graphs of the simplest isothermal cross-sections of ternary systems. Combinations of these graphs can give any formalised isothermal cross-section.

(2) Construction of the graph of an *n*-component system (a total graph) is performed by taking the sum of the graphs of the $(n - 1)$-component systems. The number of nodes (points on the plane) of the resulting graph is equal to the number of phases in the *n*-component system. The edges of the graph are obtained by copying all edges from the source graphs of the $(n - 1)$-component systems to the graph of the *n*-component system.
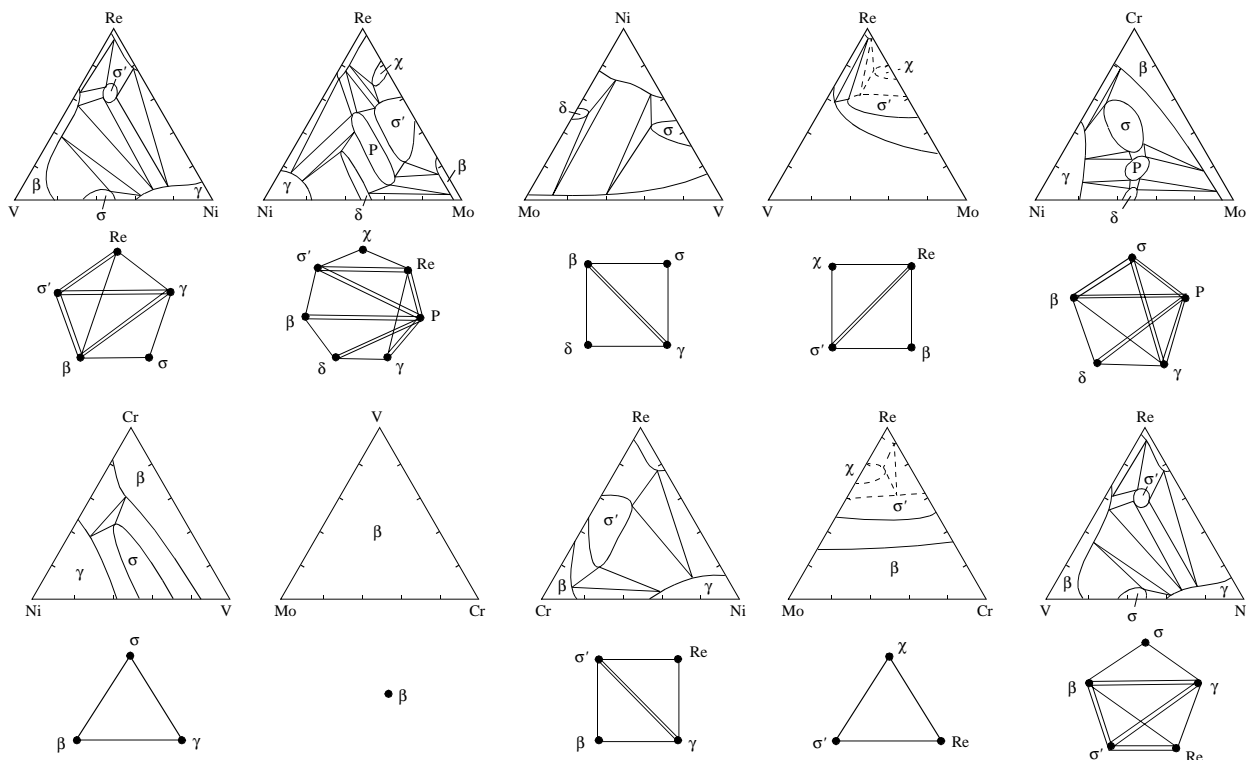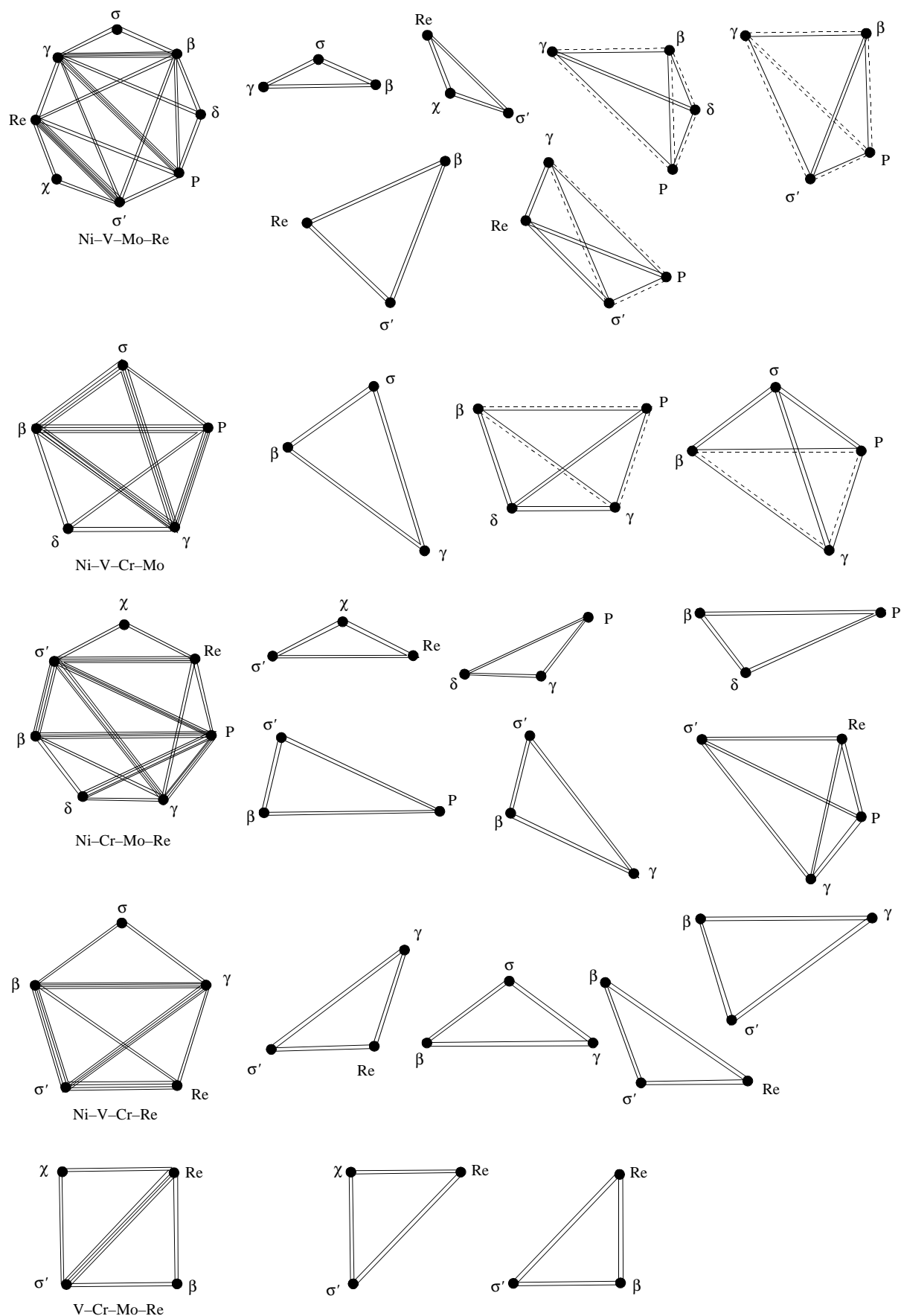

Figure 3 Ternary isotherms and their graphs in the Ni–V–Cr–Mo–Re system at 1425 K.

Figure 4 Total graphs of the quaternary systems and their decomposition into the graphs of three- and four-phase equilibria.

(3) Decomposition of the total graph of the *n*-component system into graphs of the *N*- and (*N* – 1)-phase equilibria. Moreover, this division can be performed in a variety of fashions.

In the division of a graph, it should be taken into account that phase equilibria in the (*n* – 1)-component systems provide incomplete information on all phase equilibria in the *n*-component system. Thus, the (*N* – 1)-phase equilibrium in the *n*-component

system can (i) degenerate into the *n*-component ($N - 2$)-phase equilibrium [Figure 2(*b*)]; (ii) recombine with the same ($N - 1$)-phase equilibrium to form the ($N - 1$)-phase region [Figure 2(*c*)]; (iii) participate in the formation of the *N*-phase equilibrium [Figure 2(*d*)].

Taking into account the aforesaid, the degenerated and recombined ($N - 1$)-phase equilibria should be separated from the total graph. The resulting graph will represent a collection of *N*-phase equilibria in the *n*-component system. The resulting graph completely characterises the number and composition of the *N*-phase equilibria, only if they do not form a general block. This is observed when several *N*-phase equilibria have alike ($N - 1$)-phase equilibria in a polyhedron. For instance, five phases in a four-component system can give two four-phase equilibria when two tetrahedrons come into contact by faces or three four-phase equilibria when three tetrahedrons come into contact by two faces. In a similar way, four tetrahedrons may come into contact by three faces. However, in this case, the fifth quaternary phase has no regions in the ternary isothermal cross-sections, and the equilibrium is interpreted as four-phase.

These quaternary phases are observed when a new compound that did not exist in the ($n - 1$)-component systems is formed. The method gives good results in metallic systems where the phases, as a rule, exhibit tightly packed structures. Consequently, the formation of multicomponent phases that do not occur in binary and ternary isothermal cross-sections is unlikely.

We consider the five-component Ni–Cr–Mo–V–Re system starting from the three-component systems.[1,2,4–10] Figure 3 demonstrates ten ternary isothermal cross-sections that form this quinary system and the corresponding graphs.

Information on the phase equilibria in four-component systems can be obtained from the data on ternary systems using the above algorithm. Figure 4 shows the graphs of five four-component systems (the total graphs), which were obtained by summation of the four corresponding graphs of ternary systems, and the decomposition of the total graphs into the elementary graphs of three- and four-phase equilibria.

Note that several alternative four-phase equilibria can occur in only two systems (Ni–V–Mo–Re and Ni–V–Cr–Mo). In this case, as an initial approximation, we decided on a configuration in which the tetrahedrons of four-phase equilibria form a circuit. The obtained three-phase equilibria that have no regions in the ternary isotherms are shown as dashed lines. It was found[1] that two four-phase equilibria, which come into contact *via* the three-phase equilibrium β–γ–P, and the recombining three-phase equilibrium β–σ–P occurred in the Ni–V–Cr–Mo system at 1425 K. These data are in complete agreement with the results of this work. To confirm the occurrence of the obtained phase equilibria in the Ni–V–Mo–Re, Ni–Cr–Mo–Re and Ni–V–Cr–Re systems, we experimentally examined the isothermal cross-sections of these systems.

The systems were investigated using diffusion couples, the superposition of diffusion zones and equilibrium alloys.[11,12] Scanning electron microscopy, microprobe analysis on a CAMEBAX-microBEAM instrument and X-ray diffraction analysis were used.

It was found both theoretically and experimentally that the following phase equilibria occur in the quaternary systems:

(1) β–δ–γ–P, β–γ–σ′–P, σ′–P–γ–(Re), (Re)–σ′–χ, (Re)–σ′–β and σ–β–γ in the Ni–V–Mo–Re system;

(2) β–δ–γ–P, β–γ–σ′–P and σ–β–γ in the Ni–V–Cr–Mo system;

(3) σ′–P–γ–(Re), σ′–β–γ, σ′–β–P, β–P–δ; P–δ–γ and (Re)–σ′–χ in the Ni–Cr–Mo–Re system;

(4) (Re)–γ–σ′, σ′–β–γ, σ′–(Re)–β and σ–β–γ in the Ni–V–Cr–Re system;

(5) σ′–χ–(Re) and σ′–β–(Re) in the V–Cr–Mo–Re system.

Based on the data concerning phase equilibria in the quaternary systems, phase equilibria in the quinary system can be determined. The following six four-phase equilibria occur in the Ni–V–Mo–Re, Ni–V–Cr–Re, Ni–Cr–Mo–Re, Ni–V–Cr–Mo and V–Cr–Mo–Re quaternary systems at 1425 K: β–δ–γ–P and β–γ–σ′–P in the Ni–V–Mo–Re system; σ′–P–γ–(Re) in the Ni–

V–Mo–Re system; β–δ–γ–P and β–γ–σ′–P in the Ni–V–Cr–Mo system; σ′–P–γ–(Re) in the Ni–Cr–Mo–Re system. The identical four-phase equilibria recombine. Thus, the following three four-phase equilibria occur in the five-component Ni–V–Cr–Mo–Re system: (i) β–δ–γ–P formed by equilibria of the Ni–V–Mo–Re and Ni–V–Cr–Mo systems; (ii) β–γ–σ′–P formed by equilibria of the Ni–V–Mo–Re and Ni–V–Cr–Mo systems; (iii) σ′–P–γ–(Re) formed by equilibria of the Ni–V–Mo–Re and Ni–Cr–Mo–Re systems.

In addition, there is also a three-phase region (σ′–χ–Re), which is the constituent of unknown four-phase equilibria including all these three phases. These four-phase equilibria can occur on the addition of a sixth component to the system.

Next, we consider the equilibrium β + γ (a region of chemical compatibility of fcc and bcc metals) in more detail. This equilibrium is involved in the two four-phase equilibria σ′–P–β–γ and δ–P–β–γ. Consequently, the two-phase region β + γ is limited by three-phase equilibria (δ–β–γ, σ′–β–γ and P–β–γ) in the sequence (σ′–β–γ) ←→ (P–β–γ) ←→ (δ–β–γ).

Thus, if all of the three phases (P, δ, σ′) occur in a ternary or quaternary system along with the β- and γ-solid solutions, two four-phase equilibria will occur in the quaternary system (Ni–V–Cr–Mo), and four-phase equilibria will degenerate in the ternary systems to result in the disappearance of the equilibrium β + γ (Ni–Cr–Mo, Ni–Mo–Re). If one of these phases is absent from the ternary or quaternary system, for example, the P-phase, the four-phase equilibria will not occur, and a wide β + γ region is limited by the three-phase equilibria δ–β–γ and σ′–β–γ (Ni–V–Mo). In the absence of δ- and P-phases, the four-phase equilibria do not occur, and the two-phase β + γ region is limited by only the three-phase equilibrium σ–β–γ (Ni–V–Cr, Ni–V–Cr–Re).

The results of the polyhedration of the five-component system are important. First, the polyhedration was accomplished without problems in spite of the fact that only information on ternary systems was used. Second, multiphase equilibria in a multicomponent ($n > 4$) system are unlike, because a five-phase equilibrium was absent from the five-component system. Third, it is likely that the overlapping of several blocks of *N*-phase equilibria through the regions of ($N - 1$)-phase equilibria is represented as circuits without the formation of ring configurations; this fact makes it possible to restore missing data without difficulty.

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