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## Rapid Method for Determining Ternary-Alloy Phase Diagrams

KURT KENNEDY, TIBOR STEFANSKY, GORDON DAVY, VICTOR F. ZACKAY, AND EARL R. PARKER

*Inorganic Materials Research Division, Lawrence Radiation Laboratory, and Department of Mineral Technology, College of Engineering, University of California, Berkeley, California*

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A rapid method for determining isothermal sections of ternary-alloy diagrams has been developed. Three elements are evaporated simultaneously onto a heated substrate in such a way that the composition of the deposit varies from point to point as it does in a ternary-phase diagram. An isothermal section of the Fe-Cr-Ni system prepared by the new technique is compared with one reported in the literature. The applicability of this technique to the preparation of ternary phase diagrams is discussed.

THE search for new and useful alloys is hampered by the lack of ternary-alloy diagrams. There are over 4000 combinations of three-element alloy systems that can be made from the 30 common metals. If the nonmetals such as carbon and nitrogen are included, the number of possible combinations is considerably greater. There is general agreement that a comprehensive collection of ternary phase diagrams is badly needed, but the time-consuming task of producing them by conventional metallurgical techniques has discouraged investigators. The authors have devised a new method of alloy preparation by means of which many ternary-alloy phase diagrams may now be rapidly determined.

### APPARATUS AND ITS OPERATION

The method involves the simultaneous condensation of three elements on a triangular-shaped substrate. The composition of the deposited film varies regularly from point to point, just as it does in a ternary phase diagram.

The arrangement of the three evaporating sources is shown schematically in Fig. 1, and a photograph of the apparatus is shown in Fig. 2. The entire assembly is enclosed in a 34-in.-diam stainless steel chamber that is evacuated to less than  $5 \times 10^{-6}$  Torr during evaporation. The three evaporating sources are located at the corners of an equilateral triangle, approximately 10 in. on a side. The substrate, which is identical in size and shape to this triangle, is parallel to the plane of the sources and is approximately 4 in. above it. The metals to be evaporated are solid blocks wedged tightly into cavities in water-cooled copper crucibles, and the energy needed to evaporate each metal is supplied by electron-

beam bombardment. The three electron beams are emitted from tantalum filaments located below the plane of the crucibles. This arrangement protects the filaments from contamination by metal vapors and leaves the region above each crucible free from obstructions. Suitably applied electric and magnetic fields are used to accelerate, curve, and focus the electron beams, as indicated in Fig. 1.

The power of each beam can be varied independently between 0.5 and 10 kW. Metals with widely different melting points and vapor pressures can be codeposited, and a wide range of evaporation rates can be used. The rate of evaporation from each source is measured with a Sloan model DTM-2A deposit-thickness monitor.

Ideally in a three-source unit of this type, the rate of deposition of each element would be inversely proportional to the distance from the evaporating source. In practice, however, the deposition rate does not follow this simple law because the evaporation is not taking place from a point source; also the hottest point on the liquid surface may shift during evaporation. The liquid is indented where the beam impinges. The temperature varies from a maximum at the impingement point to the melting point of the metal at the edge of the pool. Both the deviation from flatness caused by electron bombardment and the temperature gradient in the pool cause a nonideal distribution of elements to be deposited on the substrate. In materials that sublime, the electron beam tends to dig a wedge-shaped cavity, and thus destroys the hemispherically symmetrical evaporation pattern. This causes the composition contours in the deposited film to deviate somewhat from that predicted by the inverse-square law.

The relative amounts of the three metals deposited at any point on the substrate can be varied by suitable changes in their evaporation rates. A nearly complete ternary alloy system can be deposited by making the evaporation rates all equal, or if desired, any corner can be magnified by reducing the evaporation rates of the other two.

The substrate is a metallic foil, 0.001 to 0.002 in. thick, stretched on a spring-loaded frame that holds it tight against a slightly curved heat sink, as shown in Fig. 3. The substrate is sometimes heated in order to

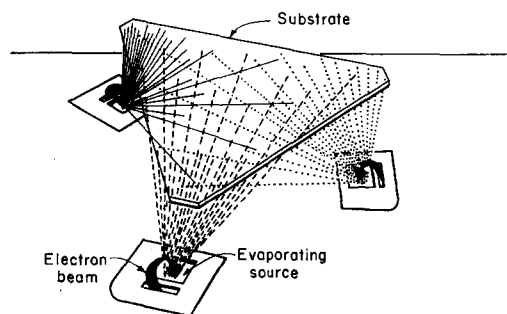


FIG. 1. Schematic of evaporation geometry.

form equilibrium phases during deposition. A heat sink assembly with two heaters can be seen in Fig. 2.

The principal criteria for the selection of a substrate material are (1) that there be no alloying between substrate and deposit at the temperature of deposition or at any subsequent annealing temperature, and (2) that there be good adherence between deposit and substrate. Stainless steel and molybdenum foil have been used successfully as substrate materials. It has been found that surface roughening, like that produced by sandblasting, is necessary for good adherence, and adherence is highly desirable for brittle deposits.

Vapor-deposited films are often badly contaminated with gases. In the present method, contamination of the deposited film is minimized by (1) using high evaporation rates, (2) starting the evaporation with the substrate protected by a shutter until the chamber has been gettered, and (3) maintaining a high vacuum (e.g.,  $5 \times 10^{-6}$  Torr).

Films more than 0.003 in. thick can be deposited in 20 min. The x-ray diffraction patterns from them are sharp, and x-ray fluorescence can be used for chemical analysis.

## RESULTS AND DISCUSSION

The Fe-Cr-Ni system was selected to illustrate the utility of the new method of alloy preparation. An isothermal section so produced is compared with an equilibrium one prepared by conventional means.

For x-ray analysis, the deposit was divided into 200 samples of equal area. The composition contour lines of a film deposited at a substrate temperature of  $760^\circ\text{C}$  were determined by x-ray fluorescence; they are shown in Fig. 4. These constant-composition lines on the deposit correspond to the linear grid in a standard ternary section. The irregular contour lines are thought to be due to the wandering of the effective center of the evaporating source over the molten pool of metal. In later experiments, this difficulty was minimized by more effective control of the electron beam. With a high-vapor-pressure metal like chromium, for example, defocusing of the beam was found to be an effective means of securing a regular deposit.

Phase boundaries were determined on a simple "present" or "not present" basis. All regions adjacent to phase boundaries were examined. The various phase boundaries are superimposed on the composition contours of Fig. 4. This section of the Fe-Cr-Ni system was redrawn on a linear composition grid to conform to standard ternary representation, with the results shown in Fig. 5. Unfortunately, the only isothermal section readily available in the literature<sup>1</sup> for this system is at  $650^\circ\text{C}$ ; it is shown in Fig. 6. The authors recognize that three-phase areas in equilibrium ternary isothermal sections are straight-sided triangles. The somewhat

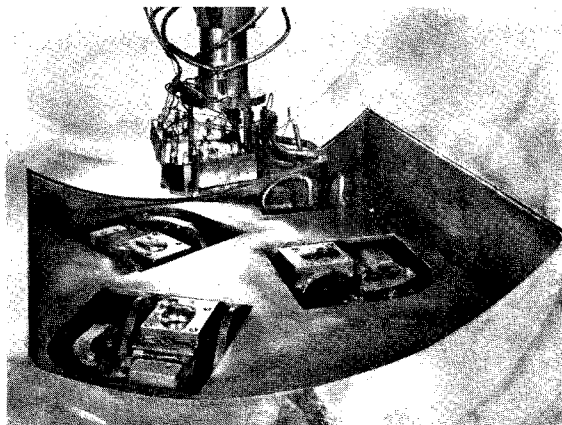


FIG. 2. Inside view of ternary electron-beam evaporator.

curved three-phase boundaries in Fig. 5 correspond to the most consistent x-ray data obtained. The boundaries may well be straight within the inaccuracies of the x-ray techniques used.

A comparison of Figs. 5 and 6 indicates that the phase relationships and the composition limits of the phases are in good agreement in spite of the large difference in temperature of the two isotherms and the normal uncertainties inherent in the preparation of ternary isothermal sections.

The authors have concluded that the new technique is suitable for the direct deposition of equilibrium isothermal sections, within certain temperature ranges, in most transition metal systems. However, there are some obvious limitations to the method. Since the as-deposited foil cools slowly within the chamber there may be phase transformations which occur during cooling. This limitation might be overcome by quenching *in situ*, and

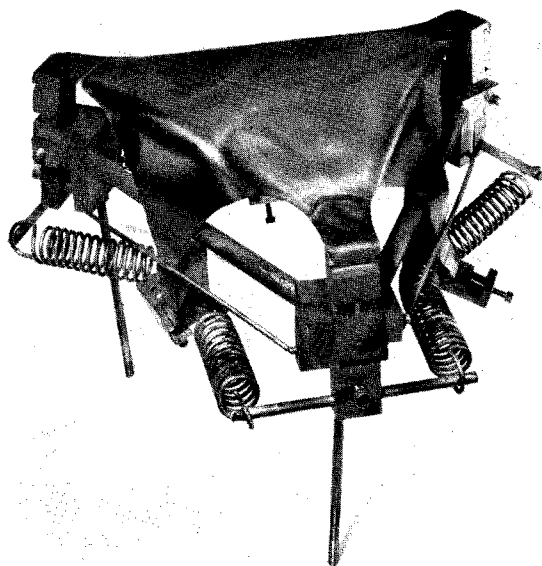


FIG. 3. Substrate-stretching assembly.

<sup>1</sup> C. J. Smithells, *Metals Reference Book* (Butterworths Scientific Publications, Inc., Washington, D. C., 1962), Vol. 1, p. 532.

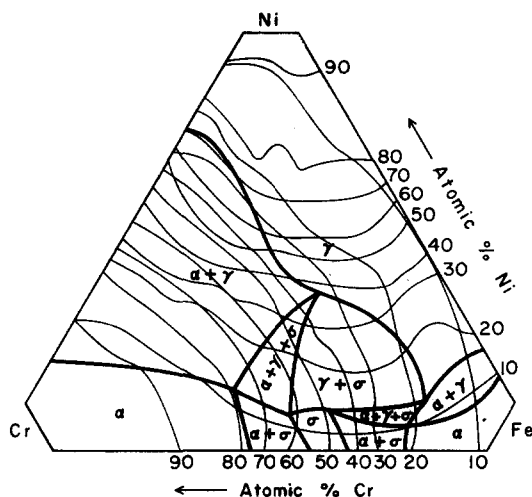


FIG. 4. Composition contours with superimposed phase map in the as-deposited film. Substrate at 760°C.

thus can be done if and when it is deemed necessary. Alternately, the foil, after removal from the chamber, can be given an equilibrium anneal followed by a quench. In addition, complete equilibrium isothermal sections can be deposited only within certain temperature limits. For a given system, there is a temperature below which solid state reactions are too slow to permit equilibrium structures to form. However, this limitation can be overcome by subsequent annealing of the film.

The upper limit of temperature is set by the lowest liquidus temperature in the system. However, the posi-

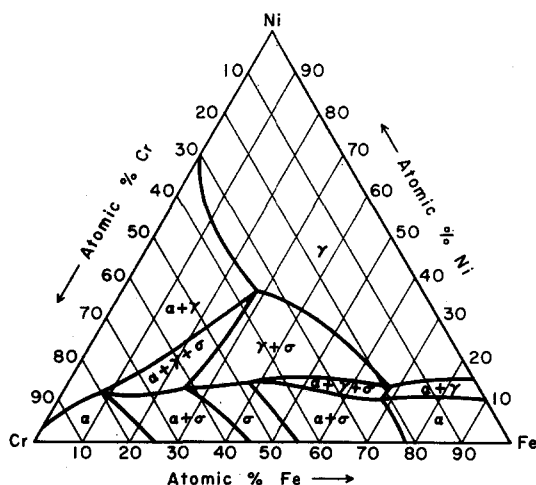


FIG. 5. Standard representation of the new ternary. Isothermal at 760°C.

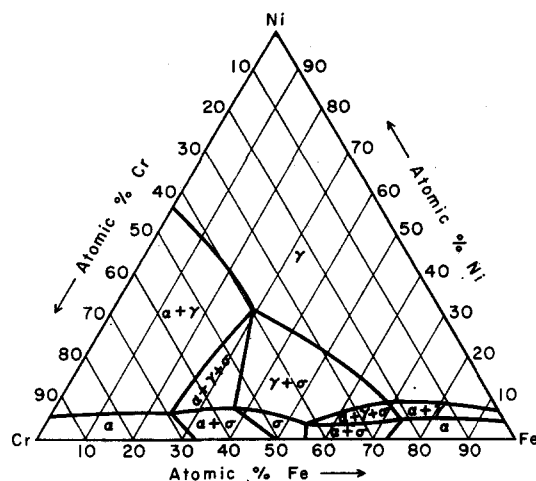


FIG. 6. Ternary reported in the literature. Isothermal at 650°C.

tions of the composition contours in the deposit can be shifted by adjusting the rates of evaporation, and by doing this it is sometimes possible to avoid the formation of liquid phases. Also, satisfactory high-temperature deposits cannot be made when the vapor pressure of the deposit is so low that significant re-evaporation occurs.

A variety of ternary deposits have been made, including the system Mo-Al-C, in which the phases  $Al_4C_3$ ,  $Mo_2C$ ,  $MoAl_{12}$ , and  $Mo_3Al$  have been identified. Also, in the Nb-Sn-Ta system, the phase  $Nb_3Sn$  was identified and found to be superconducting.

## CONCLUSIONS

Isothermal sections of many ternary diagrams can be rapidly and reliably obtained. The most time consuming step in the older, more conventional methods, namely the preparation of the numerous specimens needed for the determination of a complete ternary section, can be obviated by use of this new technique. A complete ternary alloy deposit can easily be made in a day. However, the determination of composition and structure is still time consuming, and better methods are needed for the rapid determination of composition and crystal structure.

## ACKNOWLEDGMENTS

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