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SIMULTANEOUS THREE-ELEMENT CONDENSATION

Berkeley, California

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ABSTRACT

A method is described by which three elements can be condensed simultaneously on a common substrate in such a way that the composition varies with position on the substrate. Almost all possible combinations of three solid elements can be formed in a single evaporation. The three elements are heated by magnetically deflected electron beams. The alloys and compounds formed by this method generally correspond to those made by other methods; however, many exceptions exist. Simple symmetric crystallographic phases tend to form in preference to more complex phases. The Nb-Sn, Cr-Fe-Ni, Mn-Ca and other systems of alloys made by this method will be discussed. Phases that form very slowly, such as the sigma phase in Cr-Fe alloys, may be formed rapidly by this method when certain substrate temperatures are used.

Studying all the mixtures and compounds of two or more elements by the preparation of individual samples forces the investigator to make sampling sufficiently close together so that the properties of the intermediate compositions can be inferred. A completely unknown system will require a discouragingly large number of preparations in order to fully know all its properties. For the purpose of expediting this type of investigation, a method of preparation has been devised to give continuous variation of composition with position for two or three components. This method consists of simultaneous condensation of three volatile components on a substrate such that there is a regular variation of composition with position on the substrate. The arrangement of the sources of evaporation and the substrate is shown schematically in Fig. 1. The materials to be evaporated are placed in three water-cooled crucibles located at the corners of a 10 inch equilateral triangle. Electron beams from cathodes located below the crucibles are bent 180° by magnetic fields and focussed on the material to be evaporated. The cathodes are connected in parallel to a constant current 12 kV power supply. The distribution of emission current from each cathode is controlled by filament temperature. When materials that sublime are to be evaporated, the electron beam is deflected by an auxiliary a.c. magnetic field so that the beam moves over the surface of the evaporating material rather than digging a hole in one spot.

The substrate is a 10 inch triangle of 2 mil stainless steel or molybdenum which is stretched against a slightly curved heat sink by a frame as shown in Fig. 2. This frame and heat sink are located so that each corner is directly above an evaporation source. The heat sink has three radiant heaters at each corner that can be separately controlled permitting the substrate to be either operated isothermally or with a thermal gradient.

The sources and substrate are enclosed in a 34" stainless steel tank shown in Fig. 3 and can be operated at 2×10^{-6} Torr. The evaporator and power supply were built by Temescal Metallurgical to Lawrence Radiation Laboratory specifications.

The final composition distribution of the deposit will depend on the relative evaporation rates of the sources and the position of the substrate. With equal evaporation rates from each source and the substrate 3 inches above the sources, a symmetric deposit is formed with the composition of each component varying between 2% and 95%. By changing the relative evaporation rates of sources or the height of the substrate above the sources, any composition area can be expanded. The rate of evaporation of each source is monitored by permitting a representative part of the vapors to land on a resonantly oscillating quartz crystal and measuring the change of frequency as the crystal increases its mass.

During typical operations the condensation rate is about 500 Å/sec and the thickness of a finished deposit is .002 to .005 cm. If a clean substrate is used that has been roughened by sand blasting, the deposit is adherent and can be easily handled. The crystal size of the deposit is quite small at the substrate temperature normally used but increases in size with increasing substrate temperature. The crystallographic orientation of the deposit is not generally related to the substrate and is random enough to permit x-ray diffraction directly on the deposit without removal from the substrate.

Most work has been with transition metals, however, carbon, aluminum, and calcium have also been evaporated by this method. Multielement sources such as NaCl and CaF have been evaporated and lead to pseudoternaries. If each element of a multielement source does not have the same evaporation rate the crucible must be constantly fed with material of the composition to be evaporated or the composition of evaporation will continually change.

One important use of this method is the preparation of ternary phase diagrams. The Fe-Cr-Ni system is presented as an example of an equilibrium phase diagram. The deposit was made on a molybdenum foil substrate operating at 760°C in 60 minutes. A composition survey of the deposit was made by x-ray fluorescence and presence crystallographic phases determined by x-ray diffraction. Figure 4 shows the contour lines of constant composition and the crystallographic phase as they were deposited. Figure 5 shows the phase fields drawn on a linear composition coordinate.

The lowest temperature at which the formation of the σ phase is complete was found to be 760°C. The formation of this σ phase from the solid solution is very slow and normally requires annealing for days in order to complete its formation. During formation by condensation all the atoms of the deposit are at one time surface atoms and it is felt that high surface diffusion plays an important role in the relatively rapid formation of the σ phase.

Nonequilibrium compounds can also be formed by codeposition and such systems are sometimes of interest. As an example, the results representing the Nb-Sn side of a Ta-Nb-Sn deposition which was deposited on a 300°C substrate is shown in Fig. 6. The three phases present were bcc Nb, A15 Nb_3Sn and Tet. Sn. Published phase diagrams indicate that Nb_3Sn is not stable below 900°C and the stable intermetallic phase at 300°C is orthorhombic $NbSn_2$.[1] 300°C is too low to permit even surface diffusion establishment of equilibrium. Thus the phase formed is the kinetically favored phase.

One of the axes of the substrate can be a temperature gradient instead of a composition gradient. This mode of operation was used to investigate the Ca-Mn system. An intermetallic compound near the center of this binary was thought to exist but the temperature range of stability could not be estimated. The evaporation was carried out with the heat sink operating with a 300°C temperature gradient perpendicular to the line between calcium and manganese crucibles. A new phase was detected in the 50% calcium region. However, it is not yet established whether or not this new phase is an equilibrium one.

Formation of composition gradients by condensation of two or three components is a useful technique in surveying certain types of properties that vary with composition. Properties that can be measured on a small area of a thin sample, such as crystal structure, magnetic characteristics, fluorescence, luminescence, work function, and superconductivity, are adaptable to this method.

Acknowledgements

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References

1. H. J. Levinstein and E. Buehler, Trans. Met. Soc. AIME, 230, 1314-1321 (1964).

Figure Captions

1. Schematic of evaporation geometry.
2. Substrate stretching assembly.
3. Inside view of three source evaporator.
4. Composition contours with superimposed phase map in the as-deposited film substrate at 760°C.
5. Standard representation of the phases shown in Fig. 4.
6. Composition as function of position along the Nb-Sn side of a Ta-Nb-Sn deposition with crystallographic phases indicated.

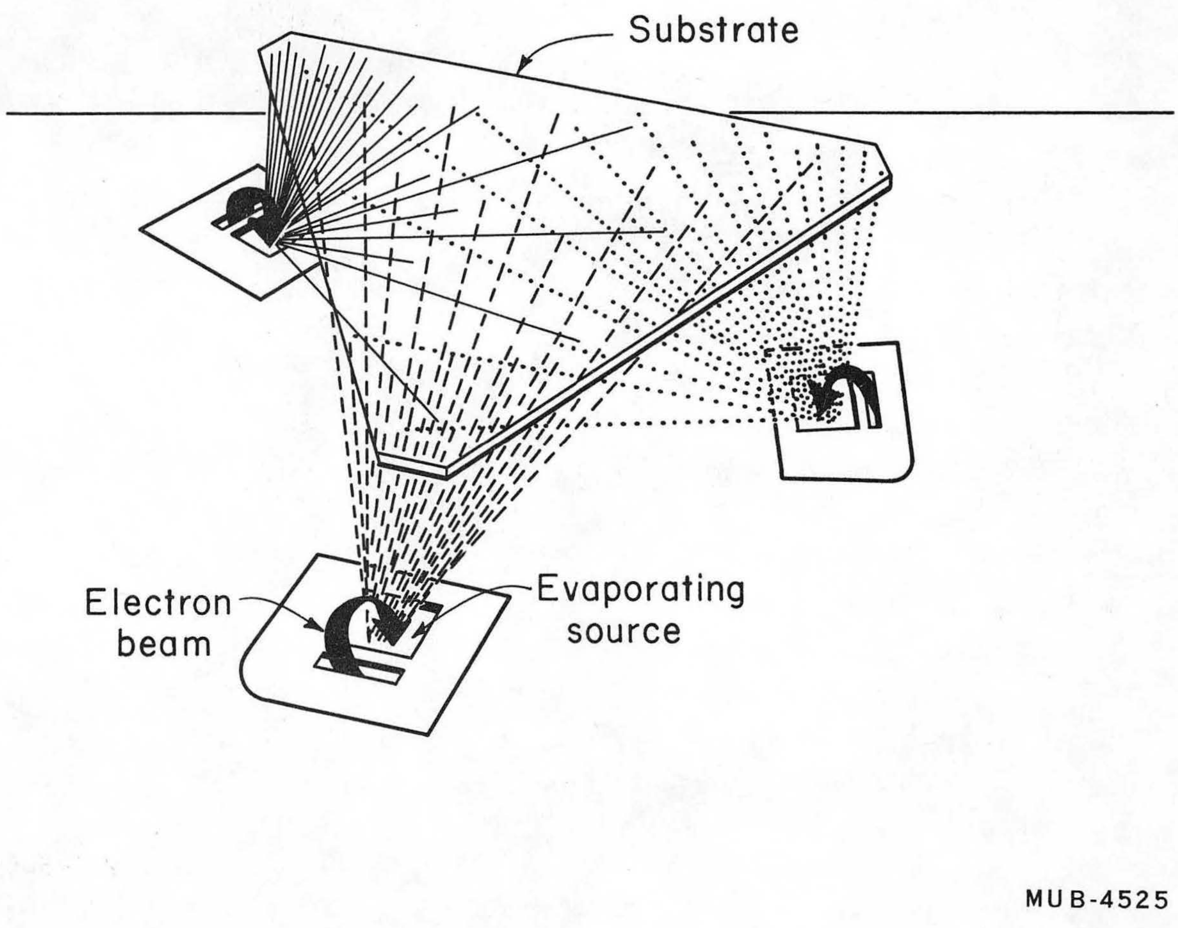

Fig. 1

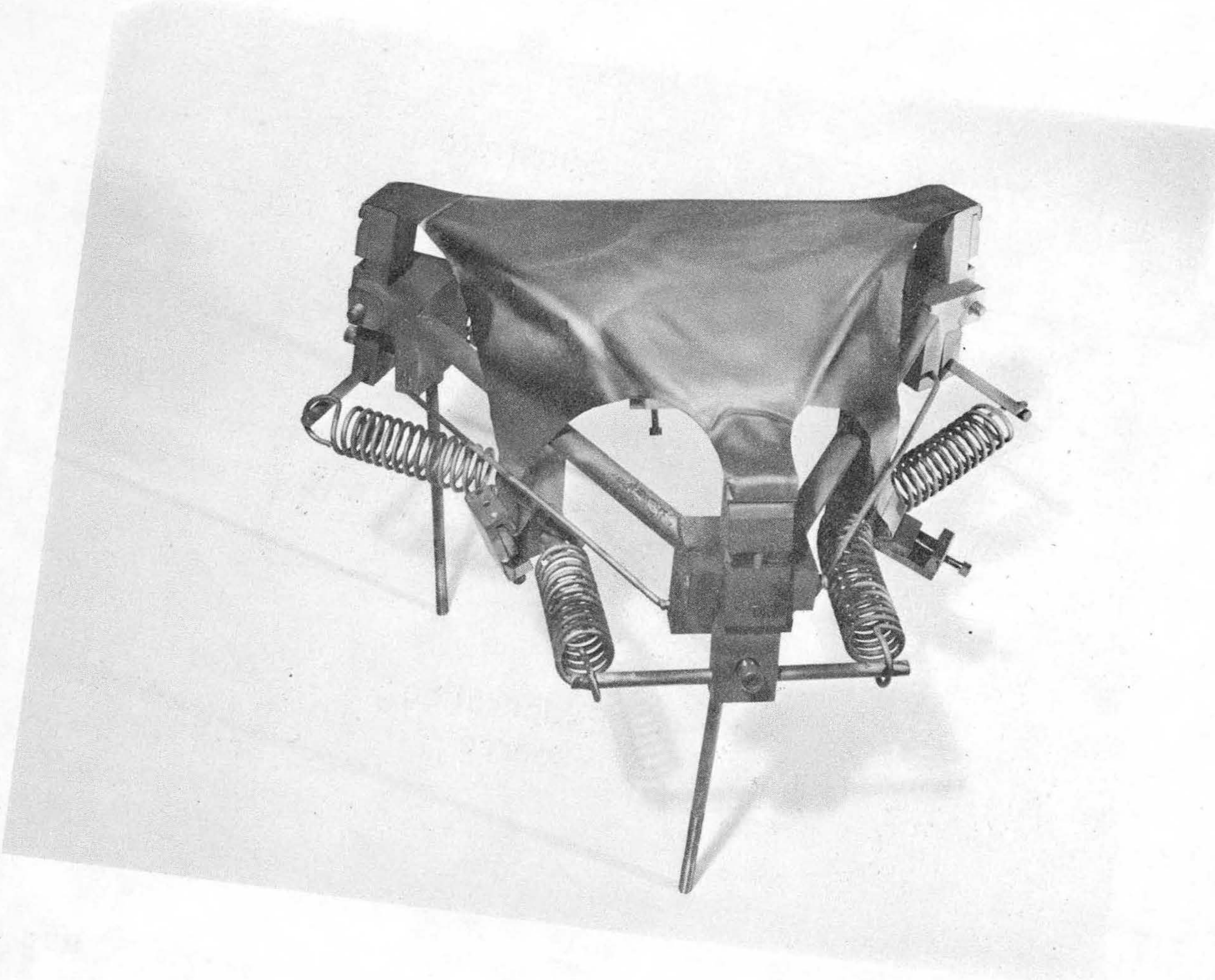

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Fig. 2

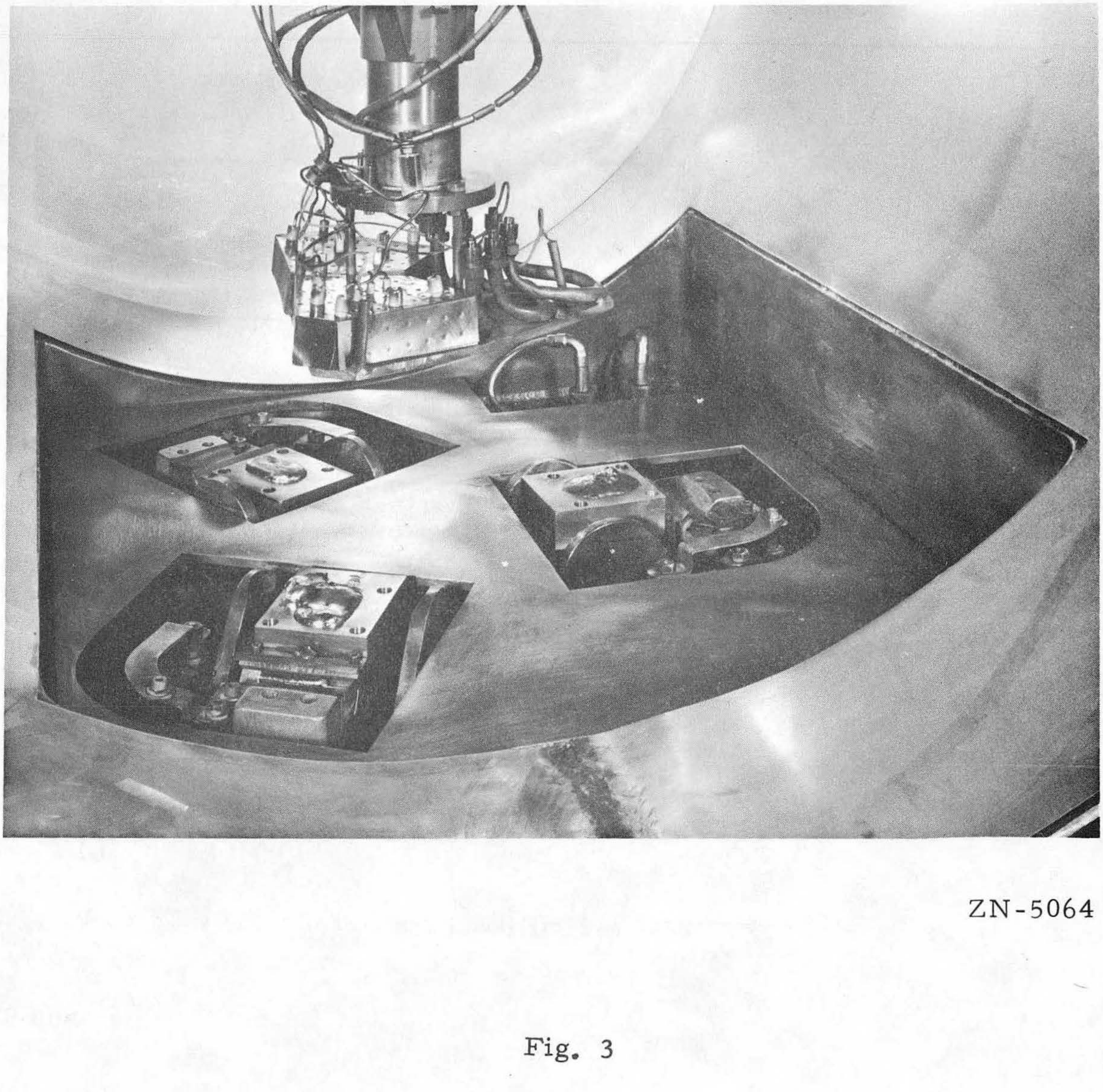

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Fig. 3

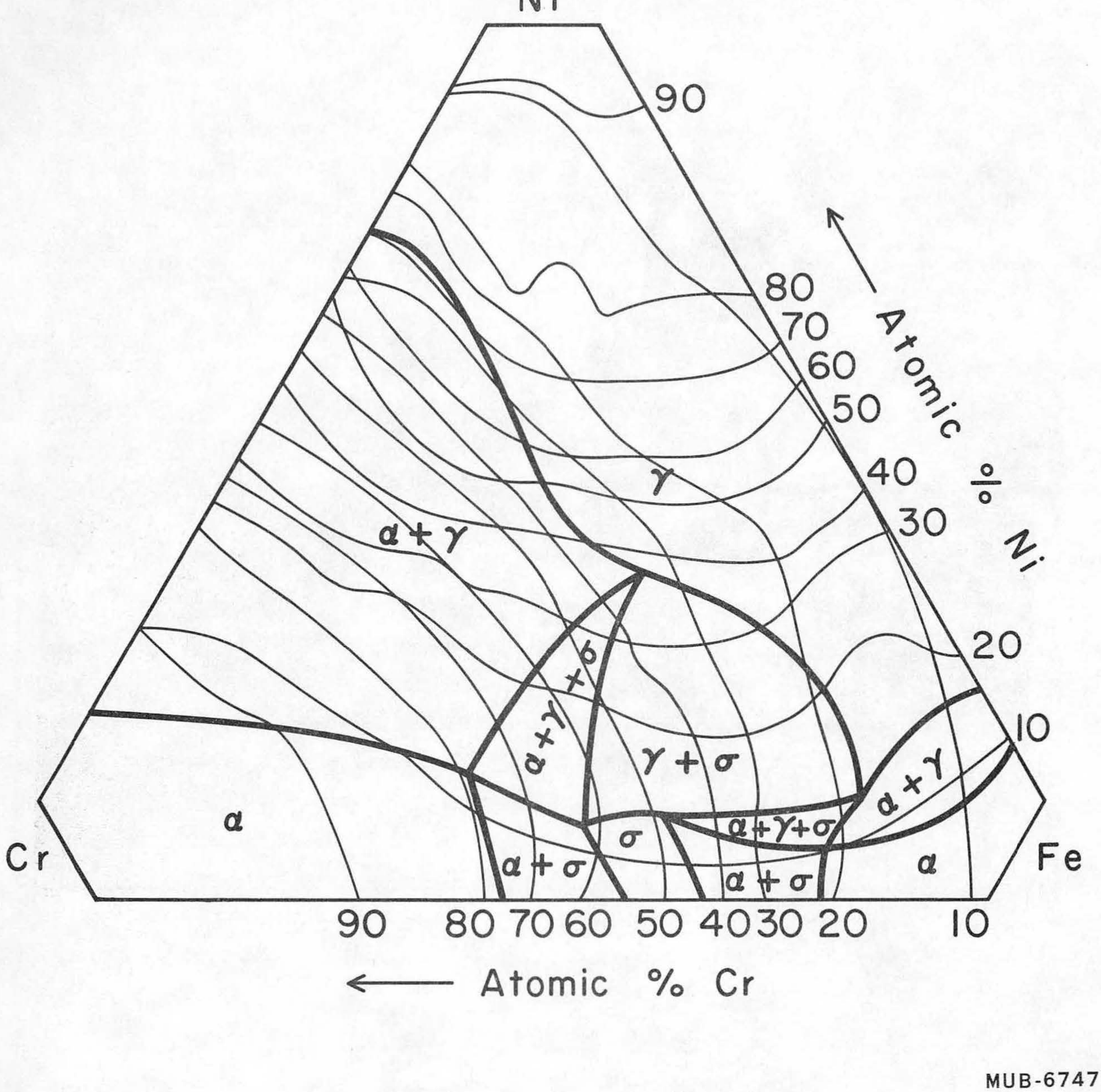
Ni
90
80
70
60
50
40
30
20
10
Atomic % Ni
γ
α + γ
α+γ+σ
γ + σ
α+γ+σ
α + γ
α
σ
α + σ
α + σ
α
Cr
Fe
90
80 70 60
50 40 30 20
10
Atomic % Cr
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Fig. 4

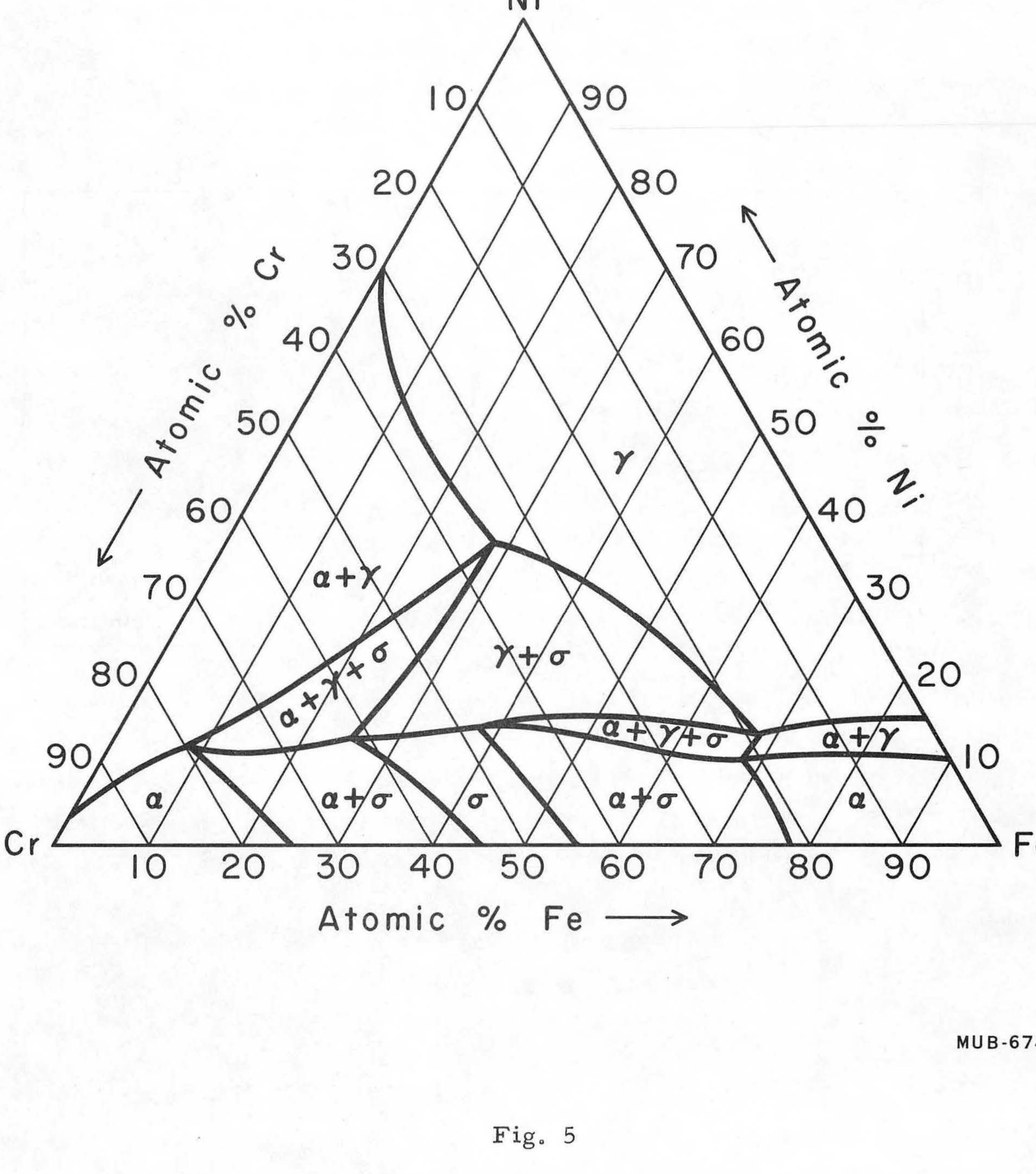

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Fig. 5

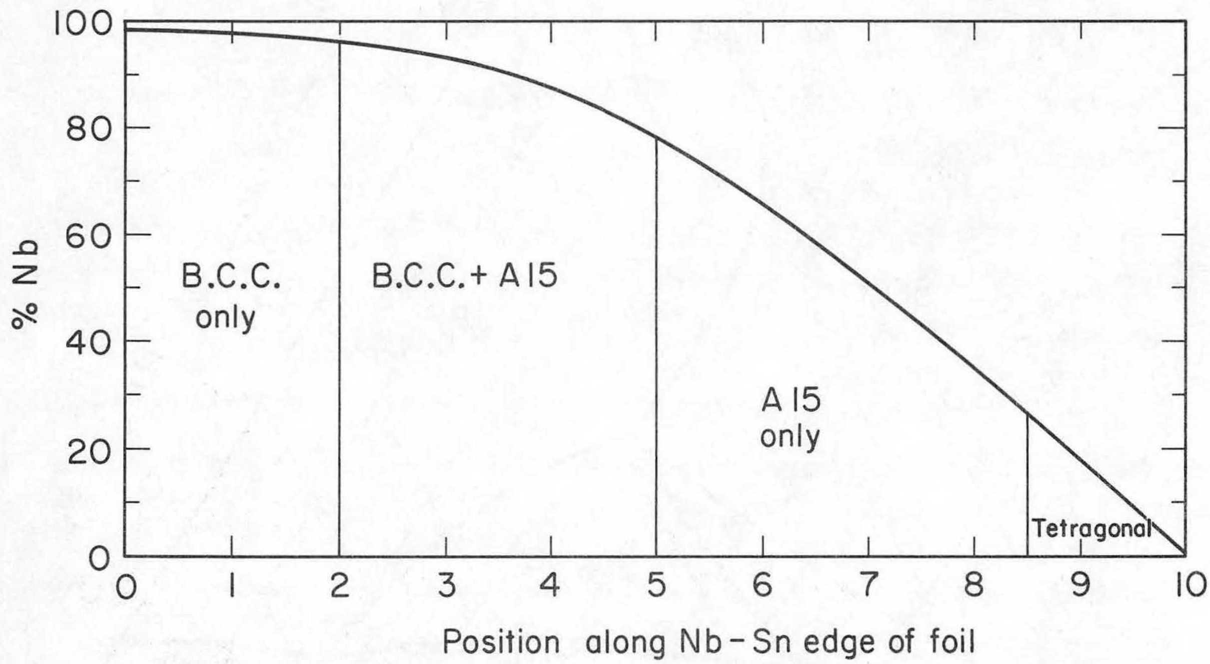

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Fig. 6