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## ABSTRACT

The binary (two component) U-Si system contains a total of seven "compounds." The most U-rich compounds are of interest to the RERTR community because they are now being employed as fuels in research and test reactors. The nomenclature used in describing these fuels and the metallurgical significance of the notations recorded may have different meanings to people from different technical backgrounds. This paper is a succinct exploration of the principles of phase equilibria and the realities of commercial fabrication as applied to U-Si alloys. It is an attempt to record in referenceable and retrievable form information of value to the continued development, application and understanding of silicide fuels.

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## I. Introduction

Discussions of silicide fuels as applied to the RERTR Program often involve considerations of the relative amounts of the various phases (distinguishable crystalline entities) present in U-Si alloys at different Si levels. This topic is being reexamined more carefully as the requirements for certain reactors exceed the U levels possible with "pure"  $U_3Si_2$ . In many ways this report is a supplement to the paper on the properties of selected U-Si alloys (Ref. 1) as well as the work of A. E. Dwight on the U-Si and U-Si-Al systems (Ref. 2). It is intended to serve as a brief exposition of the nature of binary systems as applied to an understanding of the microstructural situations likely to be encountered in utilizing U-Si alloys as fuels for nuclear reactors.

Within this paper certain rules and principles of binary diagrams are employed. More detailed discussions of these principles may be found in any textbook on physical metallurgy. Two "classic" monographs on the subject may be of interest to those who wish to pursue the subject in depth (Refs. 3 and 4).

## II. Discussion

Table I is a list of the calculated and experimentally measured compositions of  $U_3Si$ ,  $U_3Si_2$  and  $USi$ , the three most U-rich phases in the U-Si system which is shown in Fig. 1.

In all calculations and plots that follow, I have used the 3.9 wt.% Si figure for the composition of  $U_3Si$  and have rounded off the value for  $U_3Si_2$  at 7.3 wt.% Si and for  $USi$  at 10.6 wt.% Si. The densities of these phases recorded in Table I have been used as necessary.

The density figures and the microstructural conditions they represent require some amplification. The three compounds (the terms "phases," "intermetallic compounds," or "intermediate phases" may be used interchangeably) of interest here are often described as "line compounds." In the language of phase diagrams this means that within the experimental ability to define composition, a single formula and composition is assigned to each compound. They are represented, therefore, as vertical lines in the diagram. From a practical point of view -- even in terms of research activity -- it may be considered essentially impossible to produce an alloy at the exact stoichiometry of a line compound and of such atomistic homogeneity that only the "pure" phase is present. One always expects to see in a microstructure a small but finite amount of the phase to the left or the right of the compound of interest. It is even possible with minor perturbations in the distribution of the two components (U and Si in this case), that there may be regions where the phase to the left of the compound of interest is present and other regions in the same piece of material where the phase to the right of the compound is present.

The statement in the preceding paragraph regarding the possible presence of three or more phases in a two component (binary) system violates one of the fundamental tenets of phase equilibria -- Gibbs' Phase Rule. This rule states that in a binary system at equilibrium there may be at most two phases coexisting in any area of the diagram. Three phases may exist at equilibrium only along a horizontal line in such a diagram. Such horizontal lines in a binary system are called "invariant reaction lines" or "invariant reaction isotherms." The boundary conditions for Gibbs' Phase Rule as stated above is that the alloy be at equilibrium, that the pressure be constant, and the vapor phase is considered non-existent. The expression constant pressure for systems of the U-Si type may be considered to extend from very high vacuum to pressures of several hundred atmospheres.

Gibbs' Rule further demands that at constant pressure and equilibrium no more than three phases can coexist in a binary alloy under any conditions. Therefore, any discussion regarding more than two phases coexisting in a binary alloy describes, by definition, a non-equilibrium state.

To potentially complicate the story a bit more, the presence of impurities (and they are inevitably present) can lead to the existence of other phases which may or may not be distinguishable under the microscope depending on their size and the magnification employed. Impurities must also be expected to be in "solid solution" (i.e., within the crystalline lattice) in each of the phases present. The presence of such impurities in solid solution is discernible only with analytical procedures capable of accurately detecting very small quantities of a foreign species. Often such equipment and techniques are not available or, simply, do not exist.

The density figures recorded in Table I and used for the compounds of interest here may not necessarily represent the most accurate values possible. The value of  $10.9 \text{ g-cm}^{-3}$  for USi is probably accurate to  $\pm 0.1 \text{ g-cm}^{-3}$ . Values determined for  $\text{U}_3\text{Si}_2$  have varied from  $\sim 11.9$  to  $12.2 \text{ g-cm}^{-3}$ ; I have arbitrarily used the 12.2 figure. The value of  $15.2 \text{ g-cm}^{-3}$  for  $\text{U}_3\text{Si}$  represents our best value for an equilibrated alloy at 4.0 wt.% Si. We know that there is a finite amount of  $\text{U}_3\text{Si}_2$  in such an alloy but I chose not to adjust the density figure accordingly.

Nevertheless, I feel comfortable using the numbers for composition and density which I have indicated. It seems to me to be an exercise in futility to try to pin these values down to the absolutely "true" numbers. Experimental errors, analytical variability, the presence of impurities, and the question of knowing when you are at equilibrium all conspire against you in the quest for "truth."

Figure 2 is a plot of wt. and vol.%  $U_3Si_2$  as a function of Si content based on application of the tie line and lever principles for alloys at equilibrium. Likewise, Fig. 3 is a similar plot for USi as function of Si content at Si levels between  $U_3Si_2$  and USi, also for equilibrium conditions. Equilibrium is emphasized because neither of the principles may be quantitatively applied to a non-equilibrium state. Nevertheless, for arc-cast alloys in the range 7.3 to 10.6 wt.% Si and for properly heat treated (e.g., 800°C - 72 h, air cool) alloys in the range 3.9 to 7.3 wt.% Si, it is reasonable to presume that a macroscopically homogeneous melt (alloy) will approach the equilibrium condition.

For anyone interested in determining the wt. or vol.% (w/o or v/o) of phases present in the two phase fields under consideration at smaller incremental Si contents than can be conveniently read from the plots, the formulas for such calculations are presented in the Appendix.

One concern is with alloys between  $U_3Si$  and  $U_3Si_2$ . As vendors consider the fabrication of fuel elements at total U loadings exceeding those possible with  $U_3Si_2$ , they must move into the two phase ( $U_3Si + U_3Si_2$ ) field to take advantage of the higher U density possible with  $U_3Si$ . The sacrifice, however, is to accept the presence of a phase ( $U_3Si$ , which has been demonstrated to develop large fission gas bubbles at high  $^{235}U$  burnups. Our experimental data for irradiated fuels in this two phase field are somewhat limited. At ANL we have produced eight miniplates with " $U_3Si_{1.5}$ " (an arbitrary formula used to designate a composition between 3.9 and 7.3 wt.% Si). Seven of these have been sent ORNL for irradiation in the ORR. Our analyzed compositions for " $U_3Si_{1.5}$ " are 93.32 wt.% U + 5.86 wt.% Si (MEU alloy) and 93.74 wt.% U + 5.70 wt.% Si (LEU alloy). Postirradiation examination studies have only recently been initiated. We have conducted no thermal compatibility studies with  $U_3Si_{1.5}$ .

For equilibrated (properly heat treated) compositions between  $U_3Si$  and  $U_3Si_2$ , we see that at 5.41 wt.% Si we have exactly 50 vol.% of each phase. In simplest terms, compositions greater than 5.41 wt.% Si will have microstructures where  $U_3Si_2$  is volumetrically the dominant phase. Nevertheless,  $U_3Si$  may be a continuous phase even though it is a minor constituent. Therefore, even with decreasing percentages of  $U_3Si$  (as the Si content is increased), the possibility of irradiation-induced fission gas bubbles linking up in the  $U_3Si$  exists. Because of the way  $U_3Si_2$  crystallizes from the liquid state and because of the morphology of the annealed microstructures, there is evidence that the  $U_3Si$  phase is continuous (interconnecting) up to ~6 wt.% Si.

Under non-equilibrium conditions, alloys between 3.9 and 7.3 wt.% Si may be expected to contain ( $U_{ss} + U_3Si_2 + U_3Si$ ) in percentages that cannot be calculated quantitatively. It is possible to say, though, that the amounts of  $U_{ss}$  (uranium solid solution) and  $U_3Si_2$  will diminish with heat treatment (below 925°C) and the amount of  $U_3Si$  will increase, ultimately reaching the equilibrium value.

It is important to remember that  $U_3Si$  is formed by a peritectoid reaction (the horizontal line at 925°C in Fig. 1) and that any as-cast alloy in the range 0 to 7.3 wt.% Si will have some  $U_{ss}$  present in the microstructure. This is true even though the molten alloy be perfectly homogeneous and irrespective of the melting or casting techniques used. The amount of  $U_{ss}$  in an as-cast alloy may be calculated by the same procedures used to produce Figs. 1 and 2 and a plot of such data is shown in Fig. 3. In generating Fig. 3 I have simplified the presentation by assuming no solid solubility of Si in U. Formulas for calculating wt and vol.%  $U_{ss}$  in this composition range are shown in the Appendix.

The peritectoid formation of  $U_3Si$  suggests, but does not guarantee, that  $U_3Si$  is unlikely to be present in an as-cast alloy. Peritectoid reactions in metallic systems are usually sluggish and require long-time anneals to initiate and complete. As a matter of record, this author has never seen  $U_3Si$  present in an as-cast structure of a binary alloy, no matter what casting technique was used or section size (mass) produced.

For alloys heat treated below  $925^\circ C$ , the peritectoid reaction  $U_{ss} + U_3Si_2 \rightarrow U_3Si$  occurs and at equilibrium, there is no  $U_{ss}$  remaining in alloys with  $\geq 3.9$  wt.% Si. All heat-treated alloys in the composition range 0-3.9 wt.% Si will have no  $U_3Si_2$  remaining. The wt.% of  $U_{ss}$  will be a linear function of the Si content in the stated range with 100%  $U_{ss}$  at 0% Si and 0%  $U_{ss}$  at 3.9 wt.% Si. The kinetics of the peritectoid reaction have been studied by G. Kimmel, et al. (Ref. 5).

Concern has been periodically expressed about the possible existence of Si-rich compounds (e.g.,  $USi_3$ ) in U-Si alloys with  $\sim 7.5$  wt.% Si. Such a circumstance violates the rules of phase equilibria unless the molten alloy was grossly heterogeneous before freezing. Considering the melting practices at ANL as well as at commercial vendors it is difficult for me to imagine such a condition existing. During irradiation or prolonged heat treatment of fuel powders dispersed in Al, however,  $U(AlSi)_3$  will form. This is in fact the phase that it is predicted by Dwight's study of the U-Al-Si system.  $U(AlSi)_3$  is a shorthand notation for  $UAl_3$  with some of the Al positions occupied by Si atoms.

In some fuel alloy specifications, the fabricator may be required to identify the amount of each phase present in a fuel alloy as determined, for example, by x-ray diffraction analysis. It is important to recognize that under the best of conditions at least five vol.% of a phase must be present to show up in a diffraction pattern. More likely, ten vol.% is required before lines from



that phase will be evident. Also, the pattern is generated by diffraction from approximately the top 20 Å layer of each particle. Thus, depending on particle size, the diffraction pattern may represent the phases present in only a small percentage of the bulk of the sample. This is a way of saying that x-ray diffraction of powders is not a good analytical tool for the identification of the amount of each phase present in a multiple-phase alloy.

### Summary and Conclusions

A key ingredient of this paper as it applies to RERTR fuel alloy development and fabrication is simply this:

Whenever a U-Si fuel is described, a notation such as  $U_3Si$ ,  $U_3Si_2$  or  $USi$  may be recorded or spoken. For other fuels equivalent notations might be  $U_3Si_{1.5}$ ,  $U_6Fe$ ,  $U_6Mn$ , or  $U_3SiAl$ , for example. The descriptive formulas must not be taken literally. In all cases at least one other phase is present; the amount of the second phase is quantitatively related to the deliberate addition (and impurity) content of the alloy.

In all the development and fabrication work with U-Si alloys, compositions have always been selected to be on the Si-rich side of the stoichiometric compound. This choice was deliberately made to preclude the presence of uranium solid solution in the alloy and therefore in the fuel particles. The absence of  $U_{ss}$  will be the case only if the molten alloy is homogeneous before freezing and, in the case of alloys between 3.9 and 7.3 wt.% Si, after proper heat treatment.

Recognizing that perfect homogeneity and equilibrium are goals which one can approach but cannot achieve, we must always expect to have more than one phase in a fuel alloy.

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Table I. Some Data for  $U_3Si$ ,  $U_3Si_2$  and  $USi$ 

Phase	w/o Si (a)	w/o Si (b)	w/o Si (c)	Density Determined		
				at ANL (w/o $Si_3$ in Alloy)		
				g-cm <sup>-3</sup>		
$U_3Si$	3.78	3.80	3.9	15.2	(4.0)	(d)
$U_3Si_2$	7.29	7.28	7.3	12.2	(7.3)	(e)
$USi$	<u>10.56</u>	10.60	10.6	10.9	(10.6)	(e)

(a) Calculated for natural U, a.w. 238.03 used.

(b) Calculated for 20% enriched U, a.w. 237.0 used.

(c) Experimentally determined value, depleted U used.

(d) For alloy heat treated at 800°C, presumed to be at equilibrium.

(e) For as-arc-cast alloy.

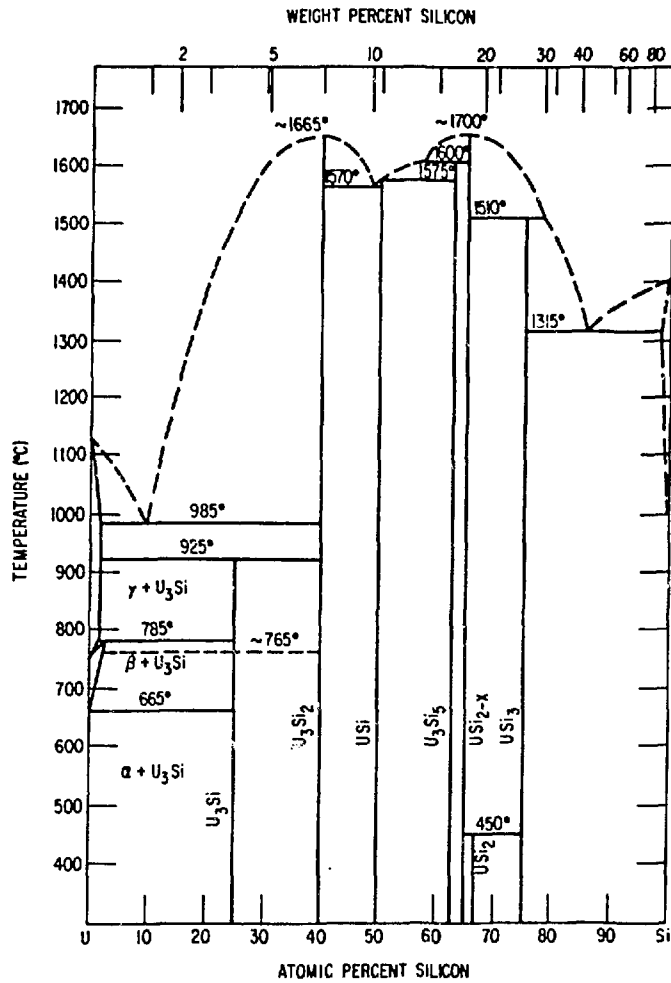


Fig. 1. U-Si Phase Diagram.

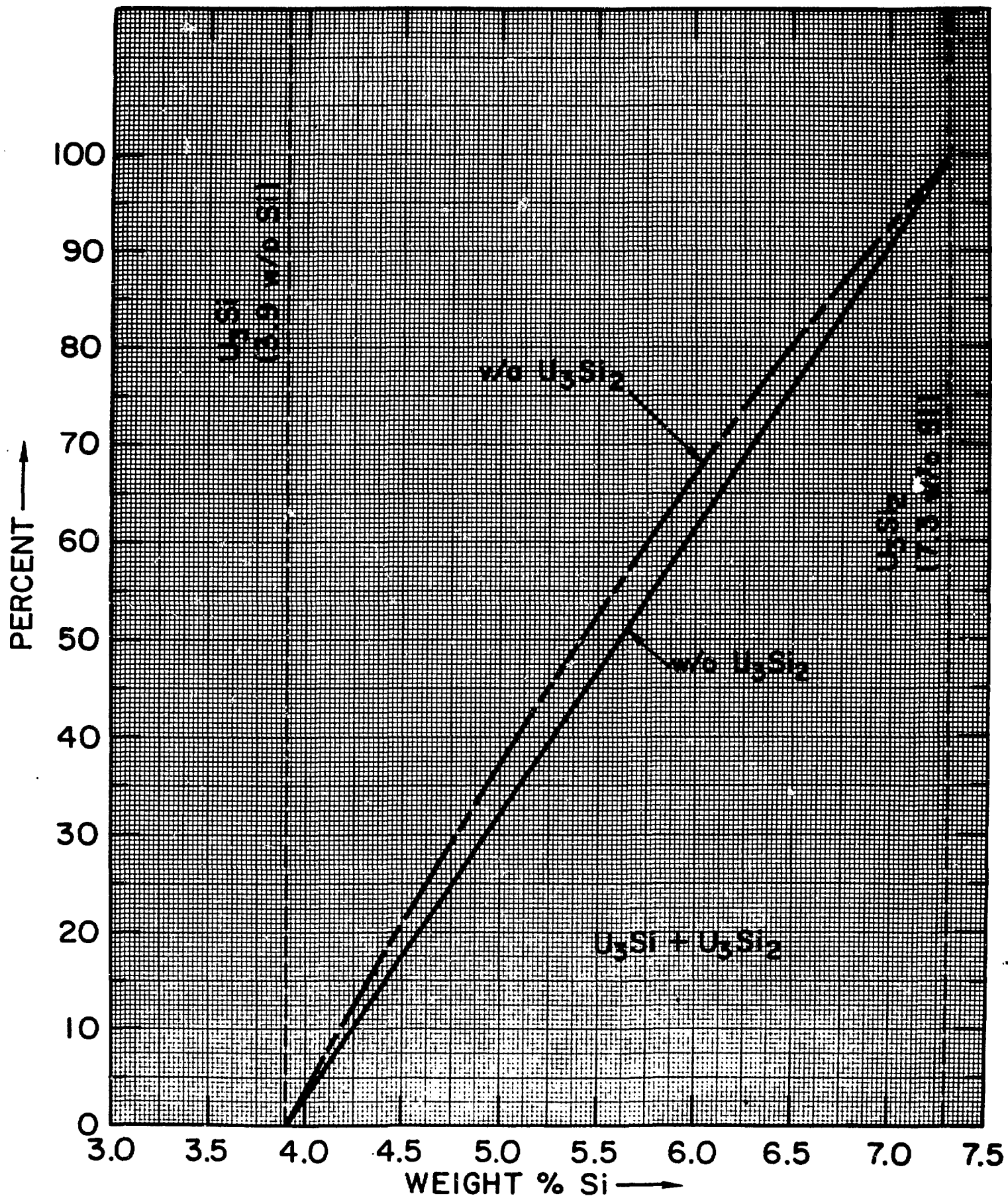


Fig. 2. Percentages of  $U_3Si_2$  vs. Weight Percent Si. Alloys at equilibrium.

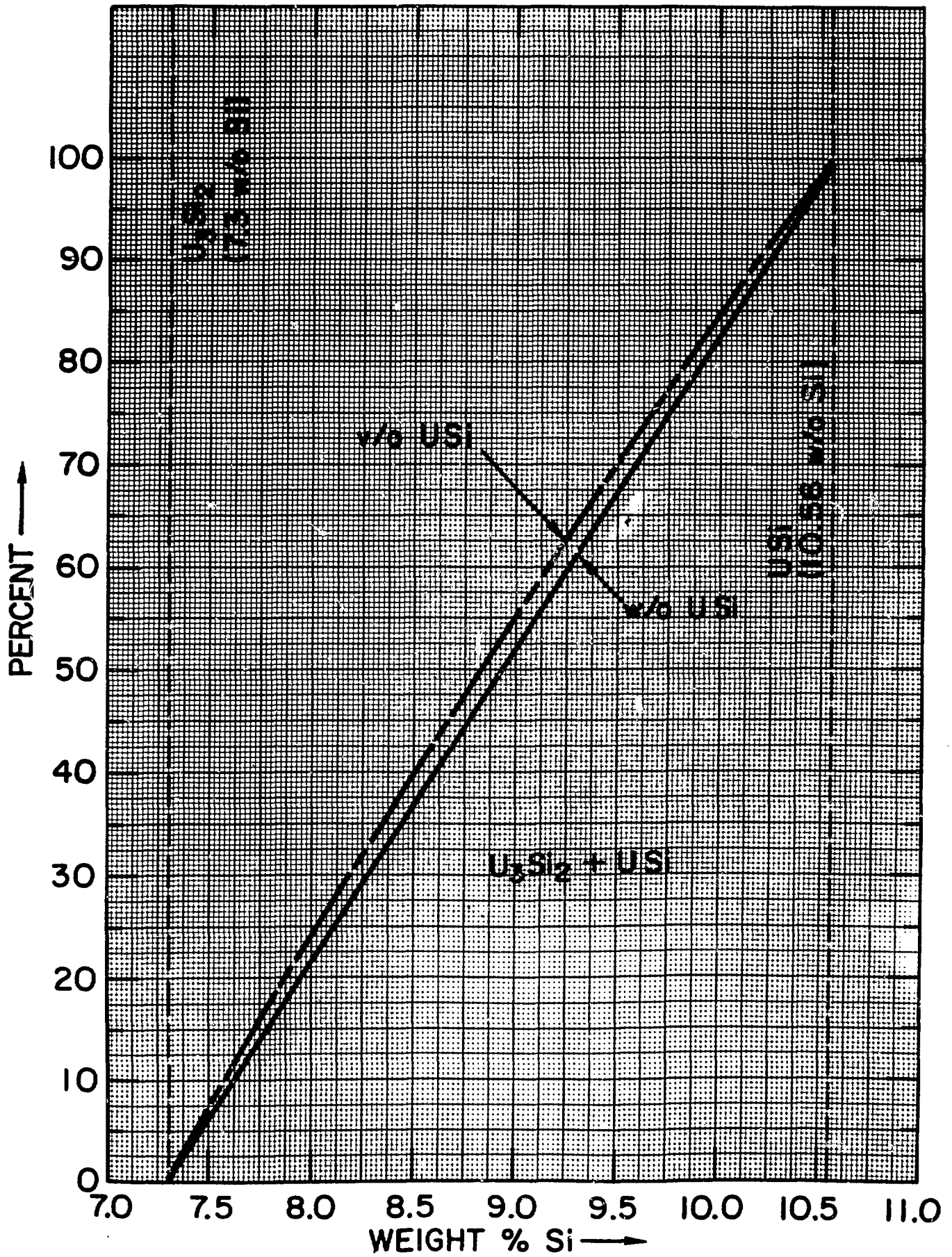


Fig. 3. Percentage of USi vs. Weight Percent Si. Alloys at equilibrium.

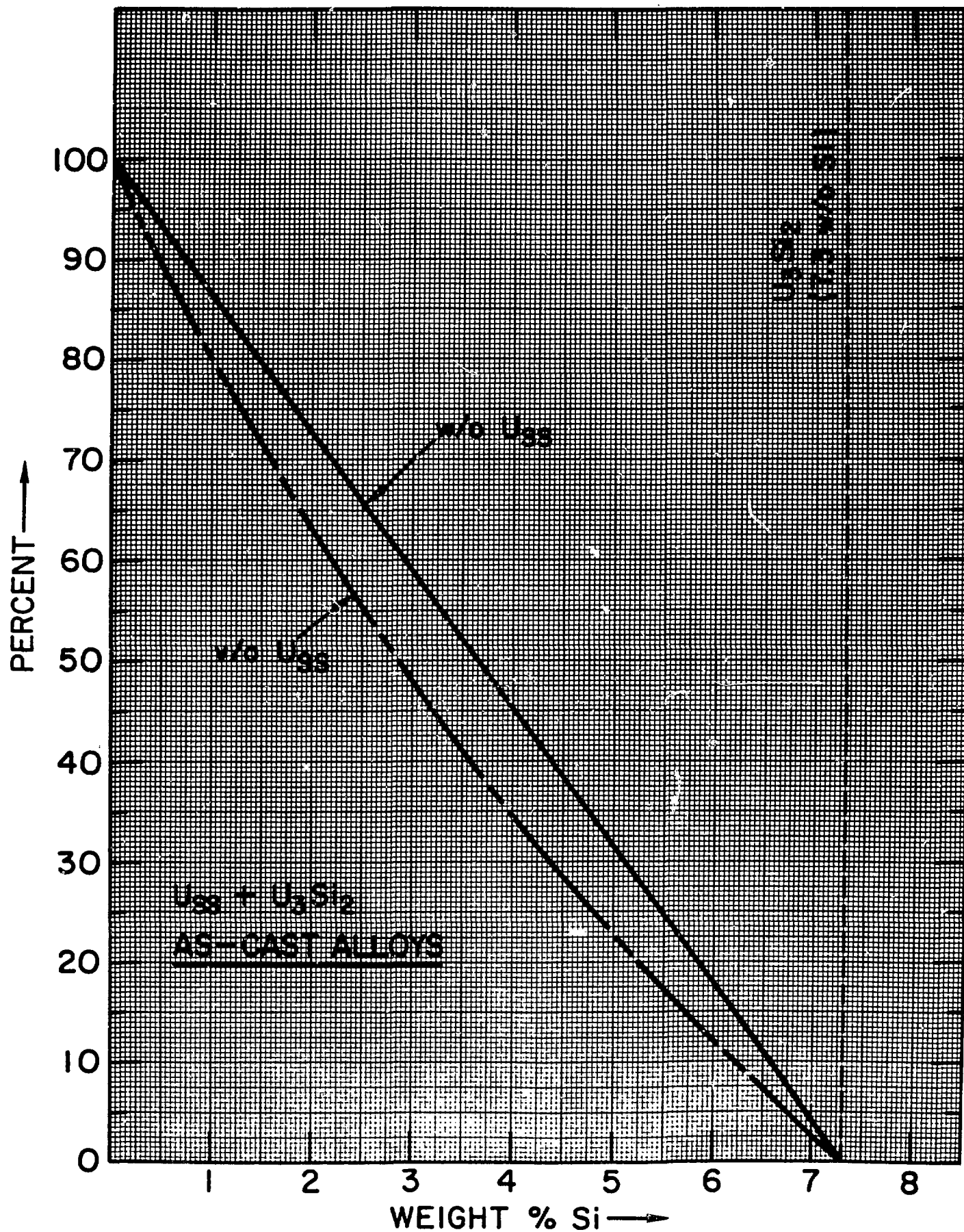


Fig. 4. Percentage of Uranium Solid Solution ( $U_{ss}$ ) vs. Weight Percent Si. As-cast alloys.

APPENDIX

Formulas for calculating percentages of phases present in the U-Si system.

Alloys at equilibrium. Densities and compositions rounded off to the first decimal. w/o = wt.%; v/o = vol.%.

1. For alloys in the two phase field  $U_3Si$  (3.9 w/o Si) plus  $U_3Si_2$  (7.3 w/o Si). Alloys annealed below the peritectoid temperature (925°C) for the "proper" time.

$$(a) \quad w/o \ U_3Si_2 = \frac{w/o \ Si - 3.9}{3.4} \times 100$$

$$w/o \ U_3Si = 100 - w/o \ U_3Si_2$$

$$(b) \quad v/o \ U_3Si_2 = \frac{\frac{w/o \ U_3Si_2}{12.2}}{\frac{100 - w/o \ U_3Si_2}{15.2} + \frac{w/o \ U_3Si_2}{12.2}} \times 100$$

$$v/o \ U_3Si = 100 - v/o \ U_3Si_2$$

2. For alloys in the two phase field  $U_3Si_2$  (7.3 w/o Si) and USi (10.6 w/o Si)

$$(a) \quad w/o \ USi = \frac{w/o \ Si - 7.3}{3.3} \times 100$$

$$w/o \ U_3Si_2 = 100 - w/o \ USi$$

$$(b) \quad v/o \ USi = \frac{\frac{w/o \ USi}{10.9}}{\frac{100 - w/o \ USi}{12.2} + \frac{w/o \ USi}{10.9}} \times 100$$

$$v/o \ U_3Si_2 = 100 - v/o \ USi$$

3. For as-cast alloys between U (0 w/o Si) and  $U_3Si_2$  (7.3 w/o Si) (alloys not heat treated)

$$(a) \quad w/o \ U_{ss} = \frac{7.3 - w/o \ Si}{7.3} \times 100$$

$$w/o \ U_3Si_2 = 100 - w/o \ U_{ss}$$



$$(b) \quad v/o \text{ U}_{ss} = \frac{\frac{w/o \text{ U}_{ss}}{19.1}}{\frac{100 - w/o \text{ U}_{ss}}{12.2} + \frac{w/o \text{ U}_{ss}}{19.1}} \times 100$$

$$v/o \text{ U}_3\text{Si}_2 = 100 - v/o \text{ U}_{ss}$$