Atomic Energy of Canada Limited

PHASE IDENTIFICATION IN THE U-Si SYSTEM

by

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Chalk River, Ontario

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ABSTRACT

Eight phases (U, U_3Si, U_3Si_2, USi, U_2Si_3, USi_2, USi_3 and Si) are reported to occur in the uranium-silicon system. This report describes the preparation of samples corresponding in composition to these phases, and the identification of each phase using the electron microprobe. The phases were characterized with respect to distribution, etching behaviour and microhardness. The results permit identification of the phases without using the electron microprobe.

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Identification des phases dans le système U-Si

par L.C. Berthiaume

Résumé

Huit phases (U, U_3Si, U_3Si_2, USi, U_2Si_3, USi_2, USi_3 et Si) se produisent dans le système uranium-silicium. Le présent rapport décrit la préparation des échantillons dont la composition correspond à ces phases et l'identification de chaque phase au moyen de la microsonde électronique. Les phases ont été caractérisées en fonction de la distribution, du comportement sous attaque et de la microdureté. Les résultats permettent d'identifier les phases sans employer la microsonde électronique.

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1. INTRODUCTION

Six intermetallic compounds are reported[1] to occur in the uranium silicon system (Figure 1). Although interest in uranium silicon alloys as nuclear fuels is limited to those containing less than 5 wt% silicon, phases of higher silicon content might be encountered due to heterogeneity in castings, selective corrosion, etc. As an aid in identifying such phases, test melts of a range of silicon concentration were prepared and subjected to chemical analysis, metallographic and microprobe examination and microhardness determination.

The results of this study are reported here and a guide to identify the phases suggested.

2. SPECIMEN PREPARATION

Six buttons, of compositions corresponding to each of the phases U_3Si, U_3Si_2, USi, U_2Si_3 (sometimes referred to [1] as β-USi_2), USi_2, USi_3, were melted under $\approx$400 Torr of argon in an arc furnace, equipped with a water-cooled copper hearth. The charge consisted of U_3Si material prepared by Eldorado Nuclear Ltd.[2] with added amounts of elemental silicon when necessary. A second button corresponding to the USi_2 composition was subsequently cast by the same method.

All buttons were melted six times, being turned over after each melt, to ensure homogeneity. Button 2 (Table 1) corresponding to the U_3Si composition was heated at 800°C for 72 hours to form the U_3Si phase from the as-cast ($U_3Si_2 + U$) phases. The remaining buttons were examined in the as-cast condition. In an attempt to obtain the USi_2 phase, one part of button 6A was heat treated at 1300°C for 12 hours while a second part was remelted in a resistance furnace, under vacuum, at 1750°C, cooled to 1500°C, held at that temperature for 2 hours and cooled slowly. The nominal compositions of all buttons, together with their analyzed compositions[3] are given in Table 1.

3. METALLOGRAPHIC EXAMINATION

Representative microstructures of samples of each button are given in Figures 2 to 7. The samples were polished mechanically using as last stage a $\frac{1}{4}$ µm diamond paste, then attack-polished with a mixture of a 30% solution of H_2O_2 and Cr_2O_3 (produced by igniting $(NH_4)_2\ Cr_2O_7$). The surface of the U_3Si sample was etched in Murakami's reagent for 75 seconds; the surface of the other alloys was not attacked consistently by this reagent. An etchant[4], employed to reveal grain boundaries in U_3Si, consisting of 3.4 g citric acid, 72 cm^3 concentrated nitric acid, 1 cm^3 48% hydrofluoric acid and 170 cm^3 water for 2 to 5 seconds, was used to provide phase contrast in alloys having higher silicon concentration.

None of the buttons was of stoichiometric composition. Two principal phases were observed in each structure.

4. MICROPROBE EXAMINATION

Microprobe analysis permits quantitative determination of elements in each phase in a sample, and thus allows identification of phases observed metallographically.

Using optimized conditions, and pure silicon and uranium standards, precision counts were made[5,6] at several points on each phase in each button. No corrections were made for absorption and atomic difference effect. The results are given in Table 1 and the phases are identified on the metallographic structures shown in Figures 2 to 7. Evidence of the USi_2 phase was found only after the second USi_2 sample was heat treated at 1300°C for 12 hours or cooled slowly after melting in a resistance furnace. Sample 6B was part of a section which separated from the main USi_2 button (6A) during arc melting; this sample was examined because of its major USi phase. Sample 6C was part of sample 6A showing segregation of two phases, USi_3 and USi.

5. MICROHARDNESS

Microhardness measurements were done on all the phases and on uranium and silicon samples using a diamond pyramid hardness identor (136°) under 50, 100 and 200 g loads and using the 50X objective in the Tukon hardness tester. The results are given in Table 2 in relation to the phases identified using the microprobe and metallography techniques. At least ten hardness readings were taken on each phase. A recognizable variation exists between some of the phases, permitting identification of the phases by their hardness. The average hardness values of each phase, when taken under a 200 g load, are given below and plotted in Figure 8. The values taken were those determined when the phases were in major concentration, except for the USi_2 phase which was never observed as the major phase.

	DPHN (200 g)		
U	- 330	U_2Si_3	- 850
U_3Si	- 244	USi_2	- 726, 647
U_3Si_2	- 626	USi_3	- 415
USi	- 701	Si	- 1052

6. DISCUSSION

No single phase alloy was produced since the intended compositions were not obtained accurately in any of the samples. In general however, the phases identified and the volume fraction of each phase present corresponded roughly to those expected from the phase diagram at the analysed silicon concentration in each sample.

In addition to the microprobe analysis three avenues are open to identify the different phases occurring in a sample; 1) reaction to etching, 2) phase distribution, and 3) hardness of the phases.

Etching Behaviour

Although U_3Si was the only phase which was attacked consistently by Murakami's reagent, some samples of USi_2 developed a tan coloration in this etchant. Thus an unambiguous identification of U_3Si by this method is not possible.

In all specimens, the phase higher in silicon exhibited a lighter shade after etching in the grain boundary etchant, thus permitting the relative silicon concentrations of the phases present to be identified.

Phase Distribution

The USi phase can be identified by its characteristic morphology when present as a minor constituent with the U_3Si_2 phase (Figure 3); such a pattern was observed on samples 3 and 4. The structure of the samples is non-uniform, being hypo-eutectic in some areas and hyper-eutectic in others. In the hypo-eutectic areas the primary USi has precipitated from the melt in a rectilinear growth spiral, illustrating the idiomorphic nature of the compound.

Microhardness

A definite variation in hardness exists between most phases. Although the ranges of the measured values overlap, their averages are distinct. The large hardness variation found for phases, when present in major or minor concentration may be attributed to internal stresses or part of the load applied on a minor phase being borne by the major phase. For identification of minor phases a smaller load was generally found to give results more representative of those for a major phase.

Should microprobe analysis not be possible for any reason, the following steps are suggested to identify the phases present in U-Si alloys:

- Determine the hardness of the major phase under a 200 g load on the largest area available and identify possible phases from Table 2. It might be necessary to go to 100 or 50 g load to avoid cracking the harder phases.

- Determine the hardness of the minor phases using a 100 or 50 g load. Identify the possible phases by reference to Table 2 and Figure 8.

- Note metallographically the contrast between the phases, to establish their relative silicon concentrations.

Combination of these observations should identify all the phases unambiguously. Minor inconsistencies in the microhardness values could result from the effect of impurities, heat treatment or cold work.

7. CONCLUSION

The eight phases (U, U_3Si, U_3Si_2, USi, U_2Si_3, USi_2, USi_3 and Si) occurring in the uranium-silicon system were observed, identified and hardness tested. No single phase alloy was obtained.

It is possible to identify the phases present in uranium-silicon alloys by a combination of:

- the microhardness of the phases,
- the phase distribution (for USi in U_3Si_2),
- the relatively lighter shade of phases higher in silicon concentration when attacked with a grain boundary etch.

8. ACKNOWLEDGEMENT

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9. REFERENCES

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2) F.H. Hueston. "The Development of Production Techniques for Uranium Silicide". OPE-42. Eldorado Nuclear Limited, Port Hope, Canada. May 1967. CONF-670522-15 (67-CNA-420)

3) R.W. Ashley and P.S. Hardy. "Manual of Methods", section concerned with "Gravimetric Determination of Silicon in Uranium-Silicon Alloys". To be issued as an AECL report.

4) J.F.R. Ambler. "Metallographic Evidence for a Martensitic Transformation in U_3Si". Journal of Nuclear Materials 22, 112-114 (1967).

5) J. Baird, private communication.

6) Mrs. T. Bethune, private communication.

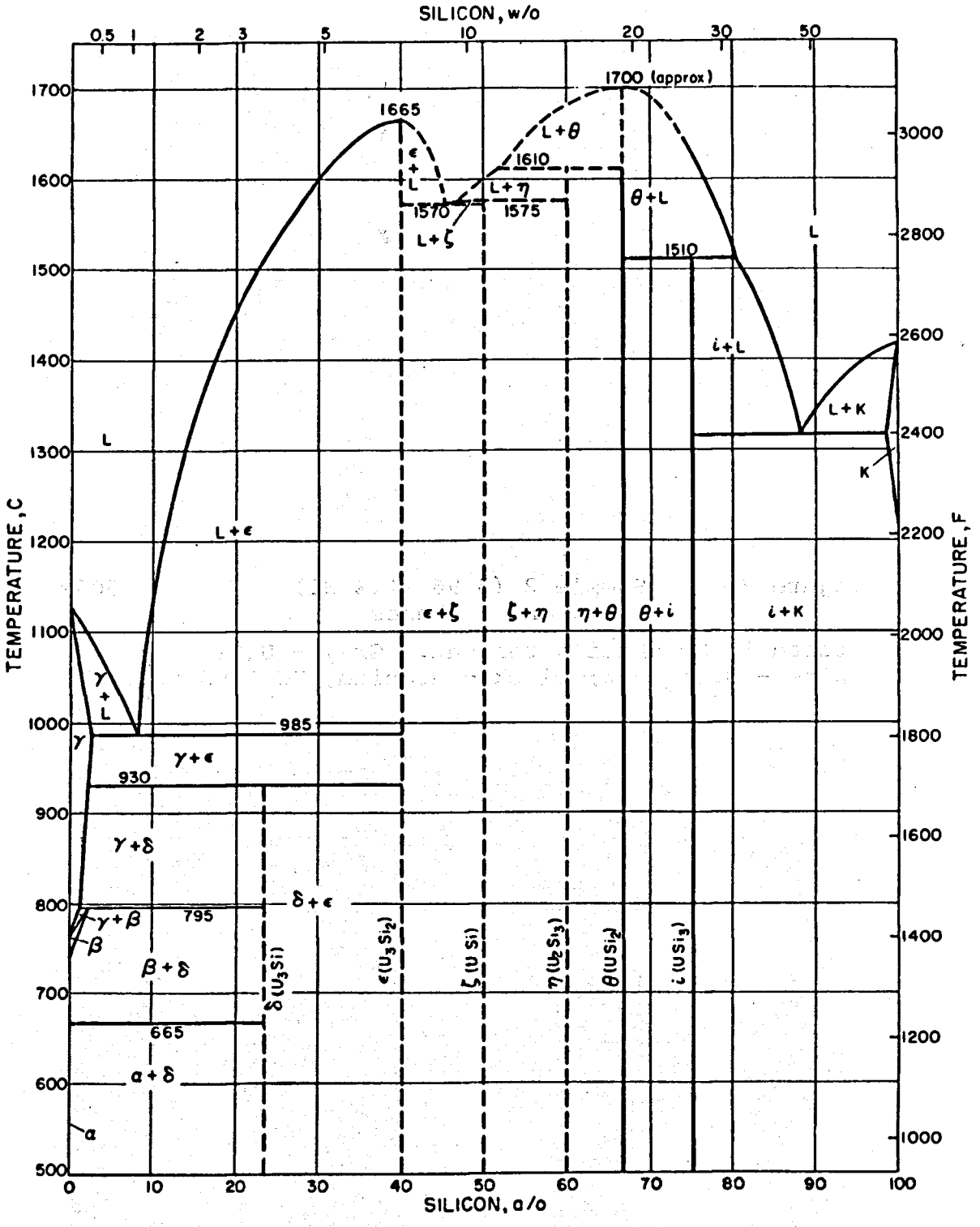

FIGURE 1 Uranium-Silicon Phase Diagram (1)

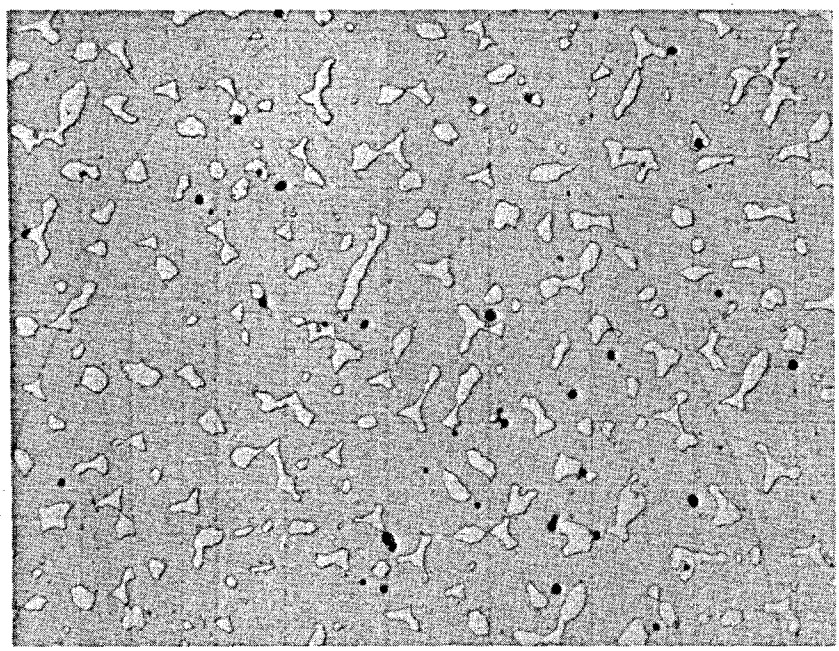

Figure 2 Sample 2 (3.96 wt.% Si) 500x
δ and ε phases

Etched in Murakami's reagent. Grey - U_3Si - δ; white - U_3Si_2 - ε; black - uranium, UC_x and UO_2.

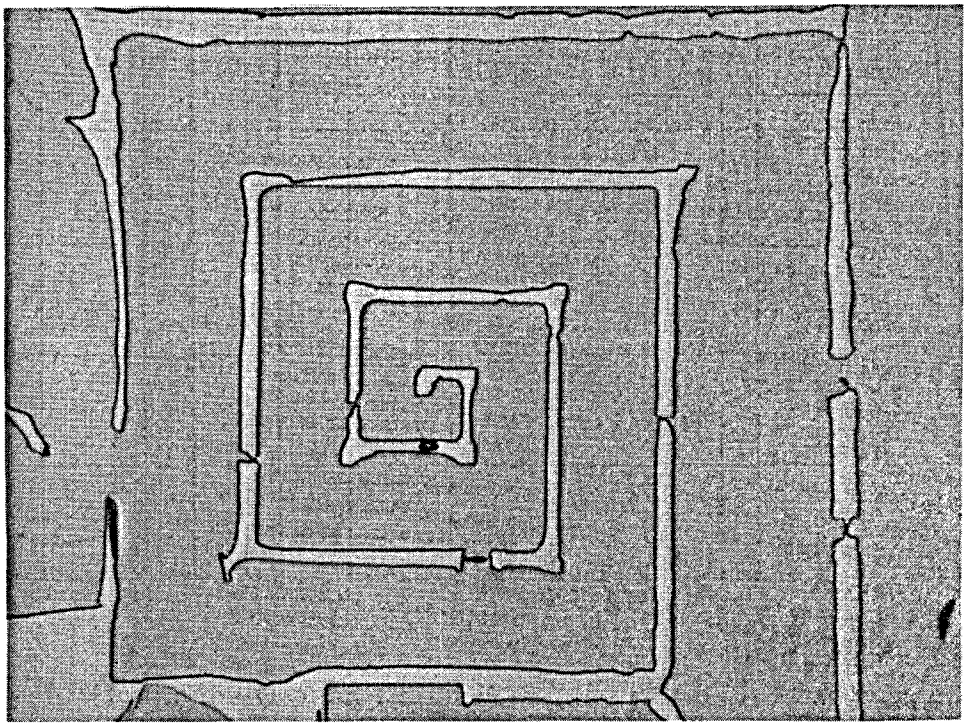

Figure 3 Sample 3 (7.82 wt.% Si) 500x
δ and ζ phases

Etched in grain boundary etch. Grey - U_3Si_2 - ε; white - USi - ζ.

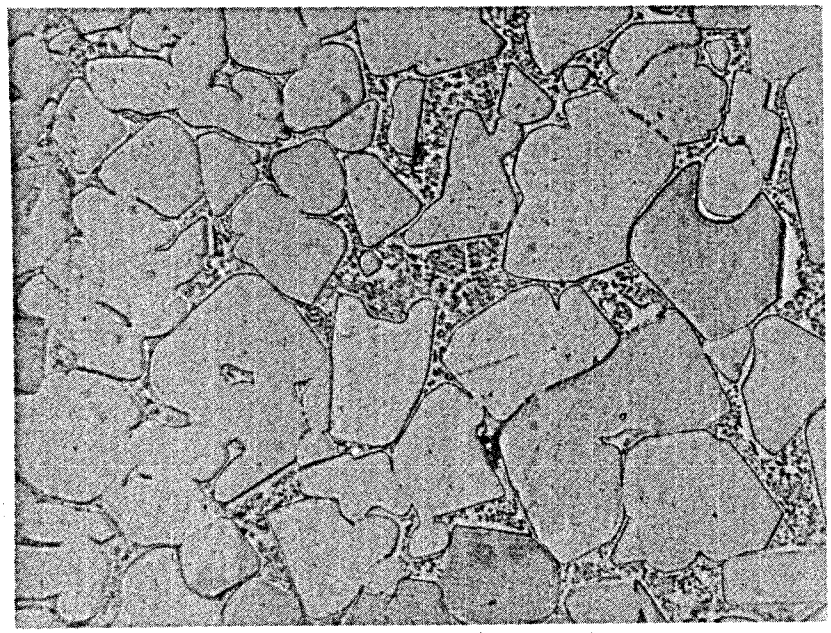

Figure 4 Sample 6B 500x
ζ phase

Section separated from the main button. Etched in grain boundary etch. Grey - USi - ζ; white with dark particles - U-Si mixture.

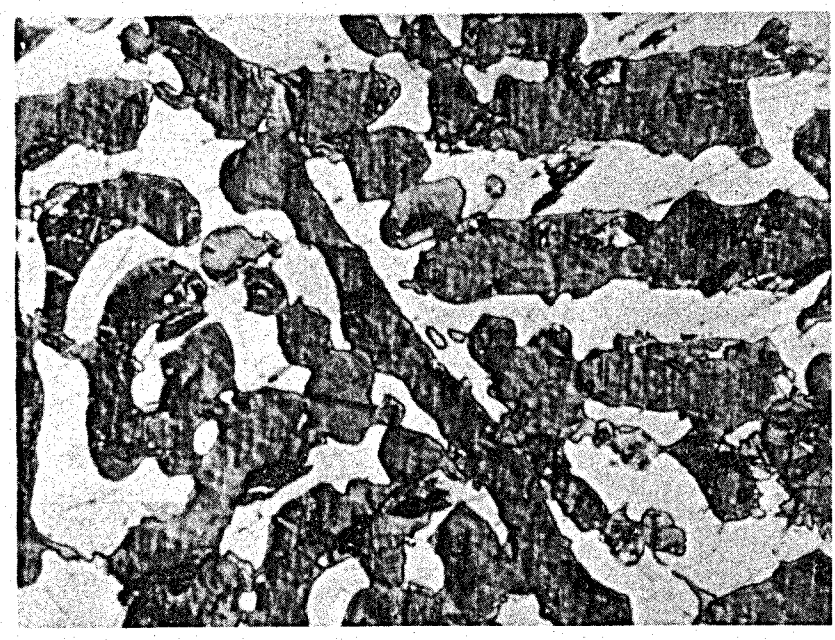

Figure 5 Sample 5 (14.34 wt% Si) 500x
η and ζ phases

Etched in grain boundary etch. Grey - USi - ζ; white - U_2Si_3 - η.

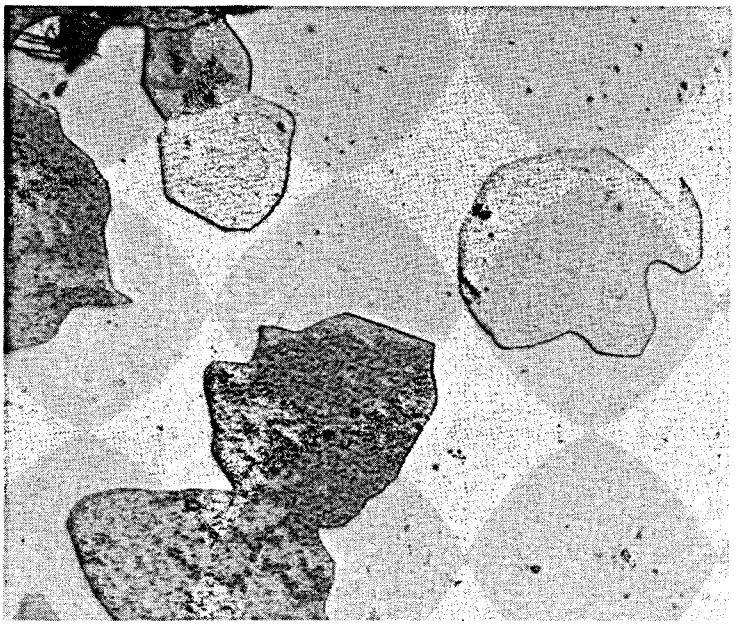

Figure 6 Sample 6D (21.5 wt%) 500x
η, θ and ι phases

Sample 6A, heat-treated at 1300°C for 12 hours. Etched in grain boundary etch. Dark grey - U_2Si_3 - η; light grey - USi_2 - θ; white - USi_3 - ι.

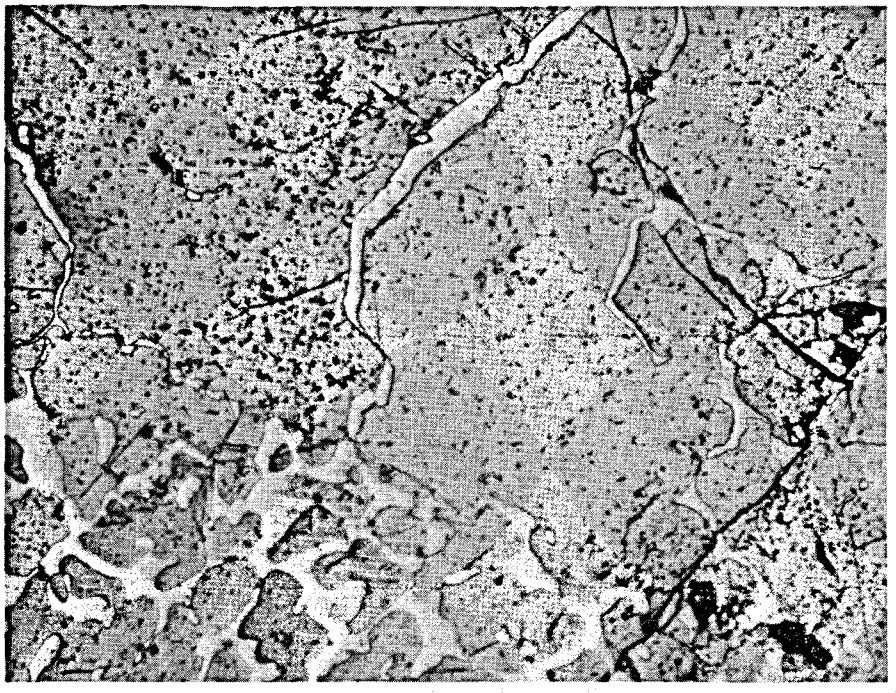

Figure 7 Sample 7 (29.76 wt% Si) 500x
Silicon and ι phases

Etched in grain boundary etch. Grey - USi_3 - ι; white - silicon rich Si-U mixture.

FIGURE 8

HARDNESS OF THE U–Si PHASES

(200 g LOAD)

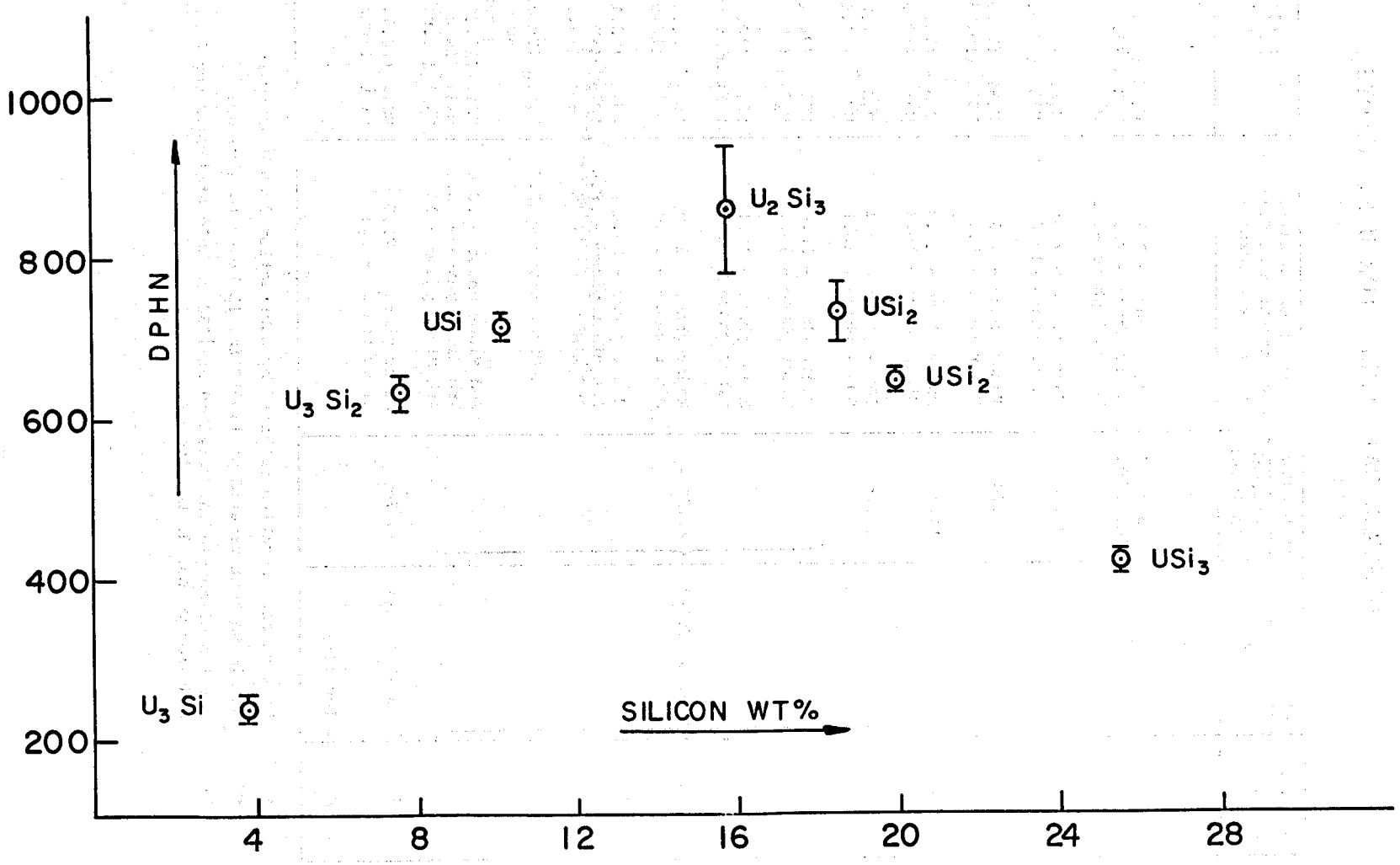

TABLE 1
GENERAL DATA SHEET FOR U-Si ALLOYS

Specimen Identity	wt% of Silicon in Uranium		Microprobe Analysis Concentration of Silicon in Phases Present (wt%)	Probable Phase Identity	Figure No.
	Intended	Chemical Analysis			
1	none (U)				
2	4.0 (U_3Si)	3.96 (Heat 192)	Major phase - 3.7 Minor phase - 7.3 Residual phase - <0.3	U_3Si (3.78 wt% Si) U_3Si_2 (7.29 wt% Si) U	2
3	7.27 (U_3Si_2)	7.82	Major phase - 7.6 Minor phase - 10.2	U_3Si_2 (7.29 wt% Si) USi (10.55 wt% Si)	3
4	10.53 (USi)	8.78	Major phase - 7.3 Minor phase - 9.9	U_3Si_2 (7.29 wt% Si) USi (10.55 wt% Si)	
5	15.00 (U_2Si_3)	14.34	Major phase - 15.8 Minor phase - 10.3	U_2Si_3 (15.04 wt% Si) USi (10.55 wt% Si)	5
6		13.7*	50% - phase - 7.4 50% - phase - 10.1	U_3Si_2 (7.29 wt% Si) USi (10.55 wt% Si)	
6A			Major phase - 26.6 Minor phase - 16.3	USi_3 (26.14 wt% Si) U_2Si_3 (15.04 wt% Si)	
6B			Major phase - 10.1 Minor phase - 1.1	USi (10.55 wt% Si) U-Si mixture	4
6C	19.05 (USi_2)	21.5*	Major phase - 26.9 Minor phase - 10.0	USi_3 (26.14 wt% Si) USi (10.55 wt% Si)	
6D**			Major phase - 25.6 1st Minor phase - 18.6 2nd Minor phase - 16.9	USi_3 (26.14 wt% Si) USi_2 (19.05 wt% Si) U_2Si_3 (15.04 wt% Si)	6
6F***			1st Minor phase - 33.9 2nd Minor phase - 20.0 3rd Minor phase - 15.8 4th Minor phase - 15.6	U_3Si_x (Eutectic with some USi_3 dendrites) USi_2 (19.05 wt% Si) U_2Si_3 (15.04 wt% Si) U_2Si_3 (15.04 wt% Si)	
7	26.10 (USi_3)	29.76	Major phase - 25.6 Minor phase - 95+	USi_3 (26.14 wt% Si) Si-U mixture	7
8	100 (Si)				

* Silicon concentration obtained by subtraction from U analysis.

** Sample 6A heat treated at 1300°C for 12 hours to give 6D.

*** Portion of sample 6A, remelted at 1750°C, held at 1500°C for 2 hours and slowly cooled, to give 6F.

TABLE 2

MICROHARDNESS OF U-Si PHASES

Phase Studied	Concentration of Phase (Specimen No)	wt% Si in Phase+	Microhardness (136° Diamond Pyramid Hardness Numbers)									Other Phase(s) Present
			50 g load			100 g load			200 g load			
			Filar Eyepiece Reading		DPHN	Filar Eyepiece Reading		DPHN	Filar Eyepiece Reading		DPHN	
			Range	Average	Average	Range	Average	Average	Range	Average	Average	
U_3Si	major (2)	3.7	100-104	101	248	140-150	148	231	199-207	204	244	U_3Si_2
U_3Si_2	major (3)	7.6	59-62	61	678	85-89	87	667	125-129	127	626	USi
	major (4)		59-61	60	701	80-85	83	733	124-125	125	647	USi
	minor (2)		65-67	66	580*	100-110	106	450*	131-139	133	571*	U_3Si
USi	major (6B)	10.1	59-61	60	701	83-85	84	717	118-120	120	701	U-Si mixture
	minor (3)		58-60	59	725	82-84	83	733	117-120	118	726	U_3Si_2
	minor (5)		56-61	58	750*	80-80	80	789*	110-124	116	751*	U_2Si_3
U_2Si_3	major (5)	15.8	50-56	54	866	72-78	76	874	104-114	109	850	USi
	minor** (6D)		55-58	56	805	83-84	84	717*	no readings (cracked)			USi_2 and USi_3
	minor*** (6F)		54-61	57	777*	83-89	86	683*	121-123	122	680*	USi_2 and USi_x
	minor (6A)		50-56	54	866	78-81	79	809	120-120	120	701*	USi_3
USi_2	minor** (6D)	18.6	58-63	60	701	87-92	89	638	115-121	118	726	U_2Si_3 and USi_3
	minor*** (6F)	20.0	59-60	60	701	84-86	85	700	124-126	125	647	U_2Si_{3+x} and USi_x
USi_3	major (7)	25.6	74-75	75	449	110-112	111	410	154-158	156	415	negligible
	major (6A)		70-76	74	461	100-120	111	410	148-152	150	449	U_2Si_3
	major (6C)		74-75	74	461	100-111	106	450	152-160	156	415	USi
	minor** (6D)		72-74	73	473	101-106	103	476	147-159	153	432	USi_2 and U_2Si_3
Eutectic + USi_3	minor***		60-66	63	637	82-85	84	717	123-126	125	647	U_2Si_3 and USi_2*
Si	major (8)		50-50	50	1010	70-71	70	1031	95-100	98	1052	none
	minor (7)		47-53	50	1010	70-71	70	1031	105-108	107	883*	USi_3
U	major (1)		90-90	90	311	125-137	131	294	170-180	175	330	none
U-Si mixture (1.1 wt% Si)	minor		75-77	76	438	93-96	95	560	140-150	145	480	USi

* The hardness of these minor phases appears to be influenced by the hardness of the other phases present, at the tested load.

** These samples were heat treated at 1300°C for 12 hours.

*** These samples were melted at 1750°C, cooled to 1500°C, held at 1500°C for 2 hours and cooled slowly.

\+ Determined by microprobe analysis.