Niobium – Silicon – Uranium

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Introduction

Missing knowledge on the interaction of uranium silicide fuel and niobium from the burn-up triggered investigation of the Nb-Si-U ternary system.
Information on the constitution of the Nb-Si-U system was provided by two cooperating research groups [1993LeB, 2000Leb] reporting phase relations for the isothermal sections at 1000°C and 850°C, which are characterized by the existence of two ternary compounds: (1) $U_2Nb_3Si_4$ ($Sc_2Re_3Si_4$ type) and (2) closely related $U_{2-x}Nb_{3+x}Si_4$, $x \approx 0.25$, with partially ordered Sm_5Ge_4 type ($Ce_2Sc_3Si_4$ type). Magnetic susceptibility and magnetization data were reported for weakly ferromagnetic $U_2Nb_3Si_4$ [1993LeB, 2000Leb]. The various experimental activities related to the constitution of the ternary Nb-Si-U system are summarized in Table 1.

Binary Systems

The binary boundary system Nb-U is from [Mas2]. The Nb-Si phase diagram was accepted in the version of [1995Sch], which was used in [2002Fer] as a base for thermodynamic assessment. The α-β polymorphic transformation of Nb_5Si_3 takes place in the temperature range 1645 to 1935°C. Nb_3Si was proposed to exist in the temperature range from 1765 to 1975°C. The system Si-U is taken from reinvestigations by [1992Rem, 1993LeB, 1998Noe], but the uranium rich part of the diagram up to 4 at.% Si is from [1965Str]. Crystallographic and melting data pertinent to the Nb-Si-U system are listed in Table 2.

Solid Phases

The crystal structures of the two ternary compounds were established from X-ray Rietveld refinements. Fully ordered and stoichiometric $U_2Nb_3Si_4$ is isotypic with the $Sc_2Re_3Si_4$ type (ordered ternary version of the Zr_5Si_4 type) additionally confirmed from neutron powder data recorded at 1.4 K [1993LeB, 2000Leb]. Single phase $U_2Nb_3Si_4$ was obtained from melted alloys annealed at 1350 to 1400°C. The second ternary phase was obtained at an off-stoichiometric formula $U_{19.3}Nb_{37.4}Si_{43.3}$ (*i.e.* $U_{2-x}Nb_{3+x}Si_4$, $x \approx 0.25$, from EMPA and Rietveld data) with the partially ordered Sm_5Ge_4 type ($Ce_2Sc_3Si_4$ type) [2000Leb]. Retarded reaction kinetics prevented the formation of a single-phase product for $U_{2-x}Nb_{3+x}Si_4$ even after long term annealing treatments (up to 3000 h) still revealing significant amounts of $U_2Nb_3Si_4$ with the $Sc_2Re_3Si_4$ type and of αNb_5Si_3. The structures of both compounds are closely related and in as-cast alloys they were observed to crystallize in long needles or plates, which separate along a common crystallographic plane [2000Leb].

Liquidus, Solidus and Solvus Surfaces

No information is available on liquidus, solidus or solvus surfaces. Alloys near the Si-U boundary with 10 at.% Si at 1000°C appeared partially molten [2000Leb]. Microstructures of as-cast alloys indicate primary precipitation of the ternary compounds $U_2Nb_3Si_4$ and $U_{2-x}Nb_{3+x}Si_4$.

Isothermal Sections

Phase equilibria have been established in an isothermal section at 1000°C [1993LeB, 2000Leb] and at 850°C [2000Leb]. The isothermal sections are presented in Figs. 1 and 2.
At 1000°C both ternary phases were observed without a homogeneity region and to form a narrow two-phase equilibrium. From the variation of lattice parameters in ternary multiphase alloys annealed at 1000°C small and in most cases negligible mutual solid solubilities among binary uranium and binary niobium silicides were concluded. This was particularly true for αNb_5Si_3 and U_3Si_2, which from XMA

showed practically no solubility for uranium and niobium, respectively at 1000°C. Even in the as-cast alloys XMA revealed less than 0.6 at.% U in αNb_5Si_3 and less than 1.5 at.% Nb in U_3Si_2. (γU,Nb) was never present in quenched alloys due to rapid decomposition below the monotectoid/eutectoid reaction temperature of the Nb-U binary revealing αU instead. According to the Si-U binary, a small region of liquid phase appears near 90U10Si at 1000°C, which solidifies on quenching the samples giving raise to non-equilibrium structures. αNb_5Si_3 was reported to be in equilibrium with the full range of the (γU,Nb) solid solution (see Fig. 1).
Phase equilibria at 850°C are characterized by the two ternary compounds: $U_2Nb_3Si_4$ and closely related $U_{2-x}Nb_{3+x}Si_4$, $x \approx 0.25$, both without homogeneity regions. There is practically no solid solubility of Nb in U_3Si_2 (maximal solubility from EMPA: 59.5U0.1Nb40.4Si), in U_3Si (maximal solubility from EMPA: 75.3U0.1Nb24.6Si) and there is virtually no Si, Nb dissolved in the uranium matrix (maximal solubility from EMPA: 99.3U0.6Nb0.1Si) in contact with the ternary phase $U_2Nb_3Si_4$. The observed two-phase equilibria: (γU,Nb) + $U_2Nb_3Si_4$ and αNb_5Si_3 + (γU,Nb,Si) prove, that there is no compatibility between U_3Si_2 fuel and niobium metal at 1000°C and at 850°C, respectively.

Thermodynamics

No experimental thermodynamic data are presently available for the ternary system. As most of the binary boundary phases engage in two-phase equilibria with stoichiometric $U_2Nb_3Si_4$, a relatively high thermodynamic stability of this ternary compound could be inferred.

Miscellaneous

The effect of 0.1 to 0.5 mass% Nb-additives on the corrosion resistance of U_3Si against water at 300°C under 90 MPa was investigated by [1993Kon]. The speed of corrosion was measured for various length of time from 100 to 1000 h. After 300 h the speed of corrosion, for instance, for the alloys with 0.4 mass% Nb was given as 0.2 $mg\cdot(cm^{-2}\cdot h^{-1})$. Niobium seems to decrease the rate of corrosion with amount (from 0.1 to 0.4 mass% Nb) and with time.
Magnetic properties of $U_2Nb_3Si_4$ in the temperature range of 5-300 K and in fields up to 2 Tesla were described with an effective paramagnetic moment $\mu_{eff} = 2.34\ \mu_B/U_{atom}$, $\Theta_p = -21$ K and a temperature independent term $\chi_o = 33.9\cdot10^{-9} m^3\cdot mol^{-1}$. $U_2Nb_3Si_4$ was said to be weakly ferromagnetic below $T_c \cong 35$ K with a rather small remanence of only $0.0088\ \mu_B\cdot U_{atom}^{-1}$. A neutron powder diffraction experiment at 1.4 K failed to reveal any magnetic contribution, which suggested that the magnetic moments were certainly smaller than ~0.3 μ_B [2000Leb].

References

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Table 1: Experimental Investigations of the Nb-Si-U Phase Relations, Structures and Properties

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1993LeB]	Arc melting of elemental ingots under argon; heat treatment at 1000-1050°C. A single phase material of $U_2Nb_3Si_4$ was obtained from an alloy annealed at 1300-1400°C for 48 h in a W-sheet vacuum furnace. Measurement range for χ: $2 < T < 300$ K; magnetization at 5 K up to 2 Tesla.	Phase equilibria at 1000°C. Determination of the crystal structures of $U_2Nb_3Si_4$ from X-ray powder data. Neutron powder diffraction of $U_2Nb_3Si_4$ ($\lambda = 0.24268$ nm, $T = 1.4$ K). Magnetic susceptibility $2 < T < 300$ K; magnetization < 2 Tesla at 5 K for $U_2Nb_3Si_4$ and $UMo_{1.25}Si_{0.75}$.
[1993Kon]	Arc-melted alloys U_3Si annealed at 800°C for 100 h. Starting materials 99.8 mass% U, chemical analysis, XPD, metallography.	Investigation of the effect of 0.1 to 0.5 % Nb-additives on the corrosion resistance of U_3Si in water at 300°C under 90 MPa (in an autoclave) from 100 to 1000 h.
[2000Leb]	Alloys prepared by arc melting or levitation melting in argon. Heat treatment at 1000°C on tungsten substrates in a high vacuum W-sheet furnace for 200 h. For equilibria at 850°C, samples within alumina crucibles were vacuum-sealed in quartz capsules and heat treated for 300 h and water quenched. Starting materials: 99.9 mass% U, 99.9% Nb, 99.9999% Si. Metallography, EMPA, X-ray powder diffraction. Neutron powder diffraction of $U_2Nb_3Si_4$. Measurement range for χ: $2 < T < 300$ K; magnetization at 5 K up to 6 Tesla.	Phase equilibria at 1000°C and at 850°C. Determination of the crystal structure of $U_2Nb_3Si_4$ and of $U_{2-x}Nb_{3+x}Si_4$, $x \approx 0.25$ from Rietveld refinements. Magnetic susceptibility $2 < T < 300$ K; magnetization < 2.5 Tesla at 5 K for $U_2Nb_3Si_4$.

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(γU,Nb)	*cI*2 $Im\bar{3}m$		[Mas2]
(γU) 1135 - 774.8	W	a = 353.35	pure U; refined at 787°C, [Mas2]
(Nb) < 2469		a = 330.04	pure Nb [Mas2]
(Si) < 1414	*cF*8 $Fd\bar{3}m$ $C_{diamond}$	a = 543.06	[Mas2]
(βU) 774.8 - 667.7	*tP*30 $P4_2/mnm$ βU	a = 1075.89 c = 565.31	[Mas2]
(αU) < 667.7	*oC*4 *Cmcm* αU	a = 285.37 b = 586.95 c = 495.48	[Mas2]
Nb_3Si 1975 - 1765	*tP*32 $P4_2/n$ Ti_3P	a = 1022.4 c = 518.9	[1995Sch]
βNb_5Si_3 2515 - 1645	*tI*32 *I*4/*mcm* W_5Si_3	 a = 997 c = 508 a = 1004.0 c = 508.1	37.5 to 40.5 at.% Si, [1995Sch] Si rich [1995Sch] Si poor [1995Sch]
αNb_5Si_3 < 1935	*tI*32 *I4/mcm* Cr_5B_3	a = 657.1 c = 1188.9	36.7 to 39.8 at.% Si [1995Sch]
$NbSi_2$ < 1935	*hP*9 $P6_222$ $CrSi_2$	a = 481.9 c = 659.2	[1995Sch]
USi_3 < 1510	*cP*4 $Pm\bar{3}m$ Cu_3Au	a = 403.53	[1992Rem]
USi_2 < 450	*tI*12 $I4_1/amd$ $ThSi_2$	a = 392.2 c = 1415.4	(metastable), [1992Rem]
α_1, USi_{2-x} < 1710	*tI*12 $I4_1/amd$ def-$ThSi_2$	 a = 394.23 c = 1371.2	$USi_{1.88}$ 65 at.% Si, [1992Rem]
α_2, USi_{2-x}	*oI*12 *Imma* def-$GdSi_2$	a = 395.3 b = 392.9 c = 1365.6	at 64 at.% Si, [1992Rem]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
α_3, USi_{2-y}	*oP*6 *Pmmm* (?) distorted AlB_2	*a* = 389.3 *b* = 671.7 *c* = 404.2	(U_3Si_5-o2) at ~ 63 at.% Si, [1992Rem]
α_4, USi_{2-y}	*oP*6 *Pmmm* distorted AlB_2	*a* = 386.4 *b* = 666.0 *c* = 407.3	(U_3Si_5-o1) at 63 at.% Si, [1992Rem]
α_5, USi_{2-y} < 1770	*hP*3 *P6/mmm* defect AlB_2	*a* = 384.75 *c* = 407.40	(U_3Si_5-hex or $USi_{1.67}$) [1992Rem]
USi < 1580	*tI*138 *I4/mmm* USi	*a* = 1058.7 *c* = 2431.0	[1992Rem, 1993LeB, 1996LeB]
USi (metastable)	*oP*8 *Pnma* FeB	*a* = 758.5 *b* = 390.3 *c* = 566.3	probably impurity (O) stabilized [1992Rem, 1993LeB]
U_5Si_4 < 1100	*hP*18 *P6/mmm* U_5Si_4	*a* = 1046.7 *c* = 391.2	Single crystal study [2006Noe]
U_3Si_2 < 1665	*tP*10 *P4/mbm* U_3Si_2	*a* = 732.99 *c* = 390.04	[V-C2, Mas2]
γU_3Si 930 - 759	*cP*4 $Pm\bar{3}m$ Cu_3Au	*a* = 434.6	[V-C2, 1965Str]
βU_3Si 762 - –153	*tI*16 *I4/mcm* βU_3Si	*a* = 603.28 *c* = 869.07	[V-C2, 1965Str]
αU_3Si < –153ºC, at –193°C	*oF*32 *Fmmm* αU_3Si	*a* = 865.4 *b* = 854.9 *c* = 852.3	[V-C2, 1965Str]
*τ_1, $U_2Nb_3Si_4$	*tP*36 $P4_12_12$ $Sc_2Re_3Si_4$ (ordered Zr_5Si_4 type)	*a* = 703.89 *c* = 1298.4	stoichiometric [2000Leb] R_F = 0.046
*τ_2, $U_{2-x}Nb_{3+x}Si_4$	*oP*36 *Pnma* $Ce_2Sc_3Si_4$ (ordered Sm_5Ge_4 type)	*a* = 0.6760 *b* = 1314.1 *c* = 693.2	at 19.3U37.4Nb43.3Si (at.%) [2000Leb]

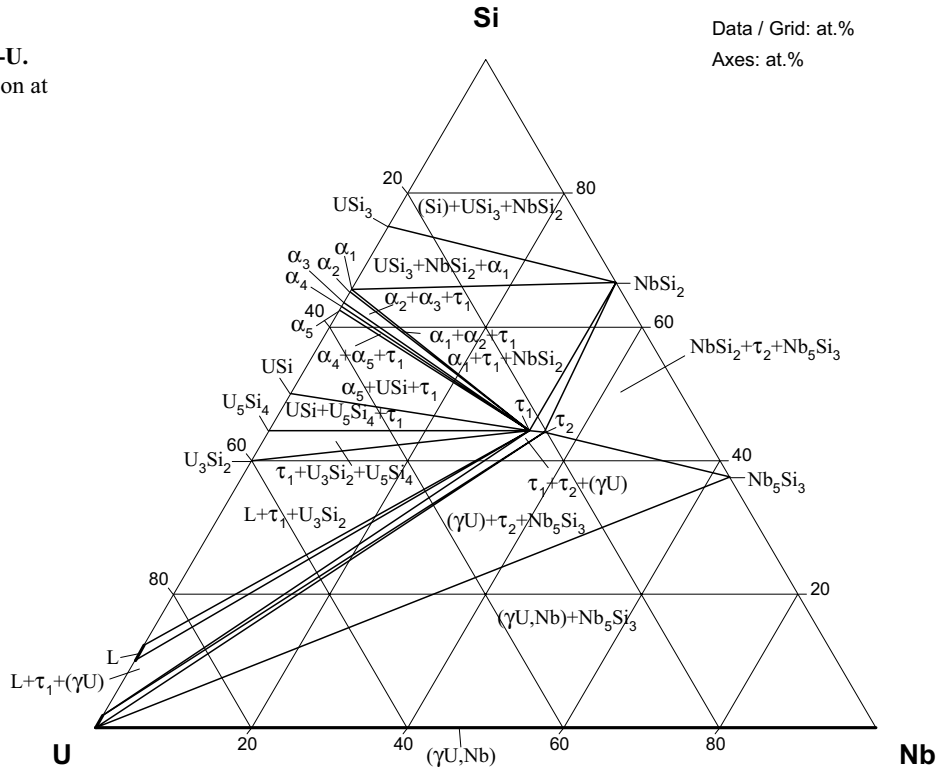

Fig. 1: Nb-Si-U. Isothermal section at 1000°C

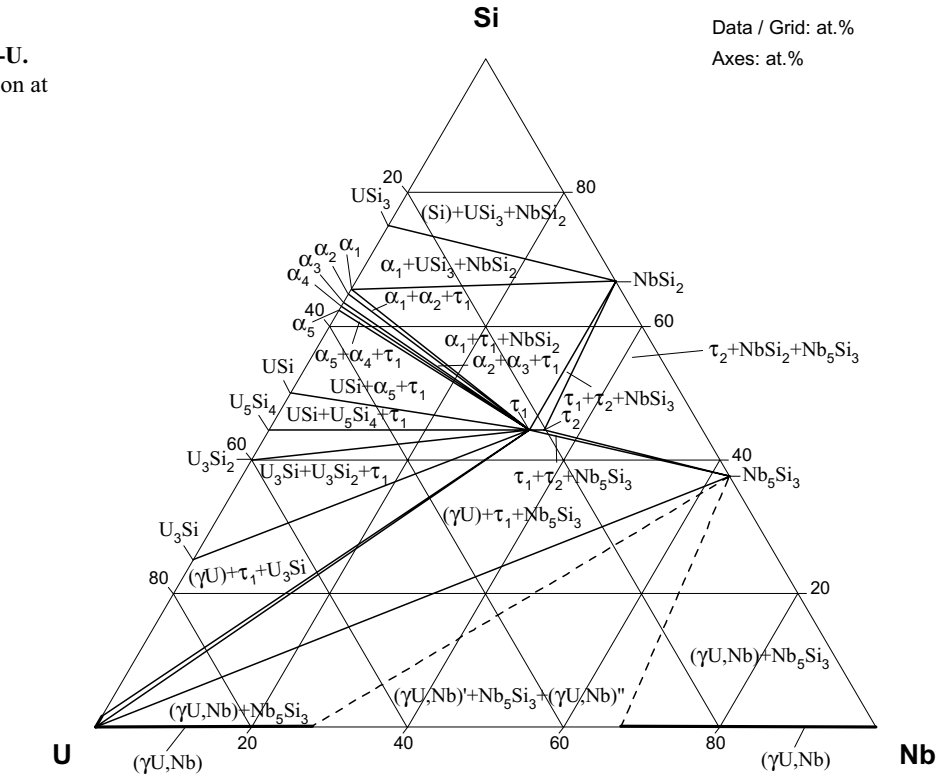

Fig. 2: Nb-Si-U. Isothermal section at 850°C