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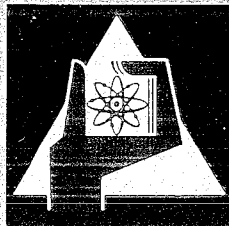
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Thermodynamics of Multi-Component Systems Containing UC and PuC

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KARLSRUHE

THERMODYNAMICS OF MULTI-COMPONENT SYSTEMS CONTAINING UC AND PuC

A review

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Isothermal and concentration sections of the phase diagrams of ternary and quaternary systems U-M-C, Pu-M-C, U-Pu-M-C, U-M₁-M₂-C, and Pu-M₁-M₂-C are described. The miscibility of UC and PuC with other binary carbides is discussed and the free enthalpies of mixing are given. The ternary and quaternary carbides and their lattice constants are compiled. The free enthalpies of formation of these compounds are estimated from the phase diagrams.

Des sections isothermes et de concentration des diagrammes des phases ternaires et quaternaires U-M-C, Pu-M-C, U-Pu-M-C, U-M₁-M₂-C et Pu-M₁-M₂-C sont décrites. La miscibilité d'UC et de PuC avec d'autres carbures binaires est discutée et des enthalpies

libres de mélange sont déduites. Les carbures ternaires et quaternaires sont assemblés avec leur constantes réticulaires et les enthalpies libres de formation sont estimées des diagrammes des phases.

Isotherme und Konzentrations-Schnitte der Phasendiagramme ternärer und quaternärer Systeme U-M-C, Pu-M-C, U-Pu-M-C, U-M₁-M₂-C und Pu-M₁-M₂-C werden beschrieben. Die Mischbarkeit von UC und PuC mit anderen binären Karbiden wird diskutiert, und freie Mischungsenthalpien werden abgeleitet. Die ternären und quaternären Karbide werden mit ihren Gitterparametern zusammengestellt und die freien Bildungsenthalpien aus den Phasendiagrammen abgeschätzt.

Introduction and explanatory notes

The mixed carbide (U, Pu)C is considered as promising nuclear fuel for fast breeding reactors. Consequently much research on the actinide carbides of systems containing these compounds has been done. The acute interest in a discussion and compilation, e.g. of thermodynamic data, is reflected in the discussions of a panel held at the IAEA in Vienna from 9-13 September 1968. This panel was concerned with thermodynamics of the binary systems U-C and Pu-C, as well as with thermodynamics of ternary systems, namely those of U-C-N, Pu-C-N, U-C-O, Pu-C-O, and U-Pu-C. These systems, therefore, will not be dealt with in detail in this paper. We refer to the Technical Report of the IAEA¹).

Moreover, it seems to be essential with regard to problems such as burn-up behaviour or compatibility studies with cladding materials,

to give a survey on the work done in the field of the constitution of the remaining multi-component systems containing UC and PuC. Furthermore we make the attempt to deduce thermodynamic data of the ternary compounds or solid solutions from the phase diagrams whereby we include the results of other papers. We try to quote characteristic publications or publications that complement or contradict each other. We base our paper on studies of the Chemical Abstracts, the Nuclear Science Abstracts, Plutonium Dokumentation of the Kernforschungszentrum Karlsruhe, as well as on the original literature. The figures are given in the original form with references. In particular, inconsistencies regarding the existence of U₂C₃ and UC₂ at certain temperatures are not considered. It can safely be assumed that UC₂ is unstable below approximately 1500 °C. The same holds for U₂C₃ above 1800 °C, e.g.⁶⁶).

Obviously small amounts of oxygen and nitrogen influence the formation and decomposition of these phases very strongly.

The multicomponent carbide systems are divided into three groups, containing

- A = A-metals (alkali and alkaline earth metals);
 T = T-metals (transition metals incl. lanthanides and actinides);
 X = B-elements (metals and non-metals of the B-groups).

A. Constitution

1. U-Pu-A-C

A = alkali or alkaline earth metals.

As yet studies of refractory carbides with alkali or alkaline earth metals have not been carried out, with the exception of systems containing Be²⁾. It appears to be of interest to know whether reactions of carbides with the very frequent fission products Cs, Sr, and Ba are possible.

1.1. U-A-C

1.1.1. U-Be-C

According to²⁾ the two-phase equilibria UC-UBe₁₃, UC-Be₂C, and UBe₁₃-Be₂C exist. No ternary compounds were observed.

2. U-Pu-T-C

T = transition metals incl. lanthanides and actinides.

The systems containing transition metals are best studied because of their technological importance. But there is as yet no clarity in the actinide-lanthanide-carbon systems relative to the extent of a monocarbide mixed crystal. This question is interesting in connection with the problem of the burn-up behaviour of carbide fuels.

The knowledge of the sections monocarbide-transition metal is important, e.g. for compatibility studies. It can be seen from the phase diagrams that UC is only in equilibrium with the VIa-metals Cr, Mo, and W, as well as with

Re and Fe. Systems containing Mn or Tc have not yet been investigated in this respect. The transition metals of the fourth and fifth group form more stable carbides than UC and PuC, those are therefore in equilibrium with uranium metal. Uranium and the transition metals of the eighth group form stable compounds with ordered structures leading to the reaction $UC + 3Me = UMe_3 + C$. It should be mentioned that carbon inclusions in octahedral voids add to the stability of these ordered structures. This leads to ternary phases that are described in section 4 of part A.

2.1. U-T-C

2.1.1. U-Y-C (fig. 1)

UC and YC_{1-x} are completely miscible, just as are UC₂ and YC₂³⁾.

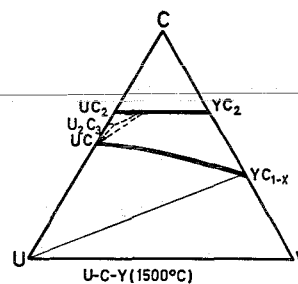


Fig. 1. Phase diagram U-Y-C at 1500 °C, ref. 3).

2.1.2. U-Ce-C (fig. 2)

At 1600 °C UC dissolves about 30 mole % of "CeC". The other carbide phases have only low solubilities⁴⁾. Ref.⁵⁾ quotes similar results with respect to the stabilization of "CeC", drawing attention to the difficulties which exist in the adjustment of the equilibrium.

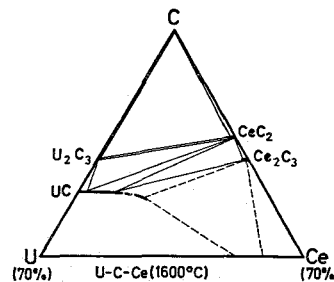


Fig. 2. Phase diagram U-Ce-C at 1600 °C, ref. 4).

2.1.3. U-Gd-C

Above 1785 °C UC_2 and GdC_2 form a complete cubic mixed crystal series, at lower temperatures a complete tetragonal mixed crystal phase. The temperature of transformation for UC_2 decreases from 1785 °C to about 1155 °C at about 65 mole % GdC_2 , increasing to 1275 °C for GdC_2 . The sesquicarbide Gd_2C_3 is soluble in U_2C_3 at 1300–1500 °C up to about $(U_{0.91}Gd_{0.09})_2C_3$ ⁶).

2.1.4. U-Th-C (fig. 3)

UC and ThC are completely miscible. According to ⁷) a miscibility gap exists in the system UC_2 - ThC_2 at 1900 °C. Ref. ⁸) shows that also UC_2 and ThC_2 are completely miscible, but that the mixed crystals cannot be quenched (fig. 4). The section UC_2 - ThC_2 then would have to be changed according to fig. 4.

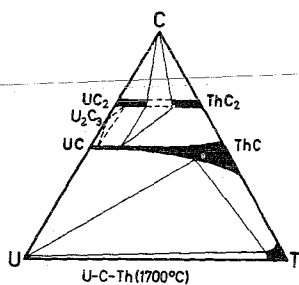


Fig. 3. Phase diagram U-Th-C at 1700 °C, ref. ⁷).

2.1.5. U-Pu-C

Not treated in this paper; ref.¹).

2.1.6. U-Ti-C (fig. 5)

The solubility of TiC in UC, rather like that of UC in TiC, is below 1 mole % ⁹). Ref.¹⁰) indicates the phase diagram of fig. 5, with a solubility of about 10 mole % UC in TiC.

2.1.7. U-Zr-C (fig. 6)

UC and ZrC are completely miscible. There is still no clarity about point x (fig. 6), according to ¹¹) it is located at 30 mole % UC at 1700 °C. Ref. ¹²) gives 70 mole % UC for 1700 °C, ref.¹³) 50 mole % UC at 1600 °C,

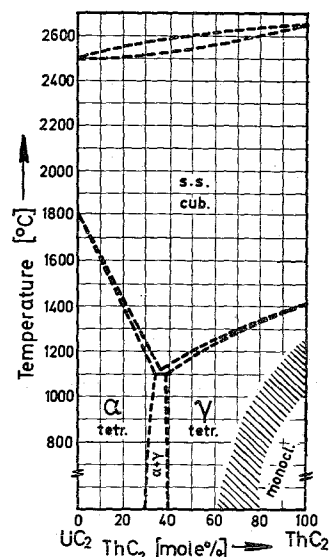


Fig. 4. Tentative diagram of the system UC_2 - ThC_2 , ref. ⁸).

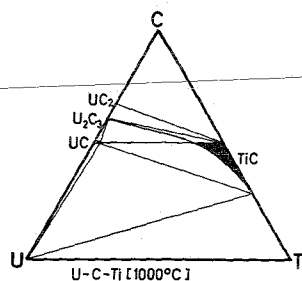


Fig. 5. Phase diagram U-Ti-C at 1000 °C, ref. ¹⁰).

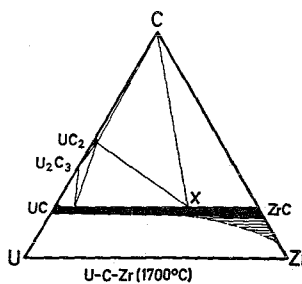


Fig. 6. Phase diagram U-Zr-C at 1700 °C, ref. ¹¹).

32 mole % UC at 1800 °C, 28 mole % UC at 2000 °C. Recently ¹⁴) has reinvestigated this system and found 39 ± 3 mole % UC at 1700 °C, 32 ± 2 mole % UC at 1900 °C and 23 ± 2 mole % UC at 2000 °C.

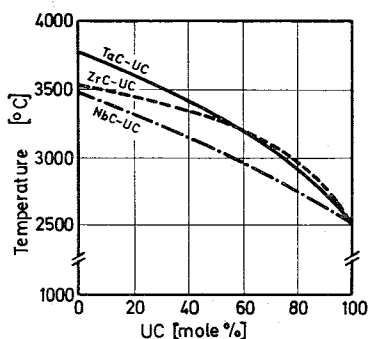


Fig. 7. Melting points in UC-containing systems, ref. 15).

2.1.8. U-Hf-C (fig. 8)

The miscibility gap in the system UC-HfC is reduced with increasing temperature (fig. 8)¹⁶⁾. At very high temperatures complete miscibility is assumed. Ref.¹⁷⁾ finds complete solubility between UC and HfC at 2000 °C. Possibly¹⁶⁾ has not obtained complete equilibrium. It can be assumed, however, that the critical temperature of segregation lies near 2000 °C in the quasibinary system UC-HfC.

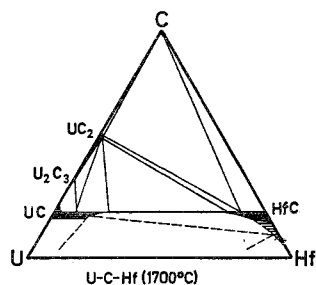


Fig. 8. Phase diagram U-Hf-C at 1700 °C, ref. 11).

2.1.9. U-V-C (fig. 9)

In the section UC-VC there is said to be slight solubility on both sides¹⁸⁾. The hypothetical phase diagram is due to¹⁹⁾. The conditions of the existence of UVC₂ are not yet known.

2.1.10. U-Nb-C (fig. 10)

UC and NbC are completely miscible¹⁸⁾. Ref.³⁾ quotes sections at 1300 °C, 1700 °C (fig. 10), and 2200 °C.

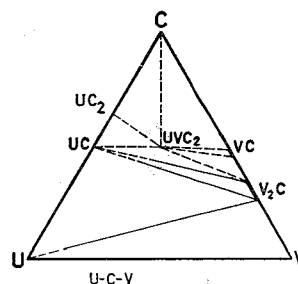


Fig. 9. Tentative phase diagram U-V-C, ref. 19).

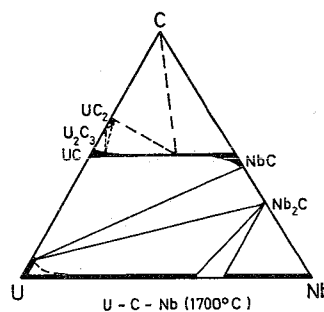


Fig. 10. Phase diagram U-Nb-C at 1700 °C, ref. 3).

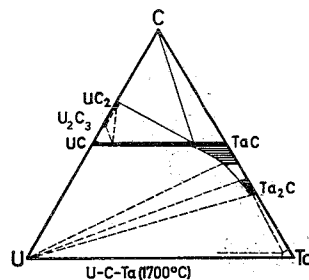


Fig. 11. Phase diagram U-Ta-C at 1700 °C, ref. 11).

2.1.11. U-Ta-C (fig. 11)

UC and TaC are completely miscible¹⁸⁾. The phase diagram of fig. 11 is due to¹¹⁾.

2.1.12. U-Cr-C (fig. 12)

No solubility of Cr in UC was observed. A ternary orthorhombic phase UCrC₂ (melting point 1625 °C) exists²⁰⁾ and another carbon-rich phase (×) is probable²¹⁾. Ref.¹⁸⁾ observed a transformation of the orthorhombic structure during the melting of UCrC₂ in graphite. The new structure is body centered tetragonal with $a=3.636$ and $c=15.739$ Å.

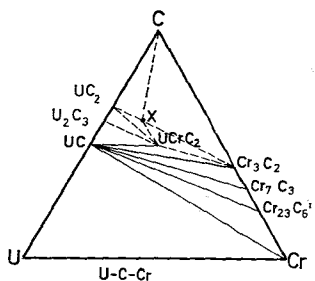


Fig. 12. Phase diagram U-Cr-C, ref. 21).

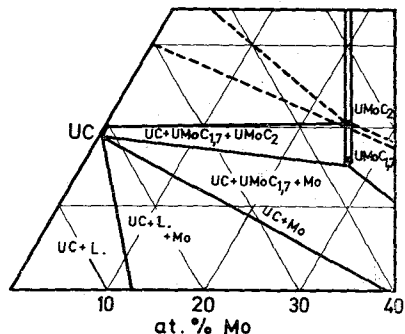


Fig. 16. Section of the diagram of the system U-Mo-C, ref. 24).

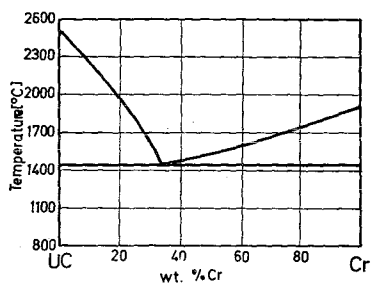


Fig. 13. Quasibinary system UC-Cr, ref. 29).

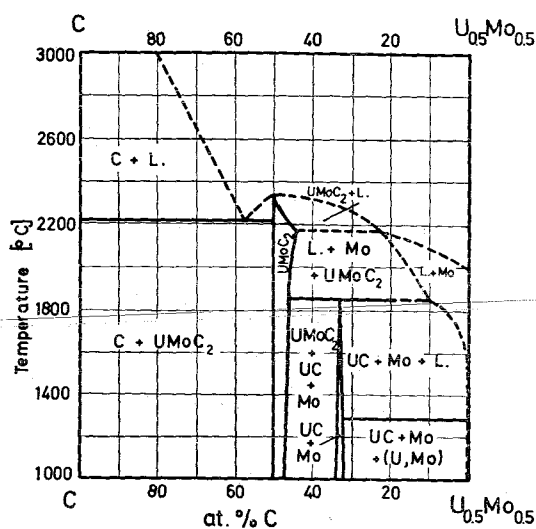


Fig. 17. Quasibinary system $U_{0.5}Mo_{0.5}$ -C, ref. 23).

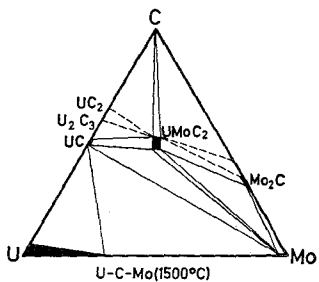


Fig. 14. Phase diagram U-Mo-C at 1500 °C, ref. 3).

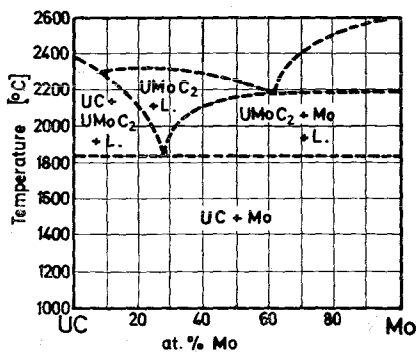


Fig. 15. Quasibinary system UC-Mo, ref. 23).

2.1.13. U-Mo-C (fig. 14)

The system is determined by the ternary phases $UMoC_2$ ^{20, 22} and $UMoC_{1.7}$ ³). Ref. ²³) gives various concentration sections (fig. 15 and 17). Accordingly ³), there is a homogeneous transition $UMoC_2 \rightarrow UMoC_{1.7}$. Ref. ²⁴) finds that the orthorhombic phase $UMoC_2$ is separated from the monoclinic phase $UMoC_{1.7}$ by a two-phase region (fig. 16).

2.1.14. U-W-C (fig. 18)

Refs. ^{3, 25}) give temperature sections at 1500 °C. The equilibria are determined by a ternary phase UWC_2 ²⁰). The solubility of W in UC is small ^{25, 26}), it results in a slight decrease of the lattice parameter (fig. 19). According to ²³) the section UC-W is similar

to that of fig. 15 for UC-Mo and is characterized by the equation $2UC + W = UWC_2 + \text{liquid}$. Ref. 27), however, mentions a eutectic system (fig. 20) for the section UC-W and an increase in the lattice parameter with solution of W in UC (fig. 21).

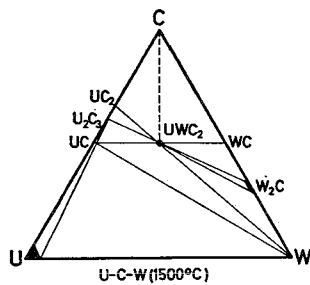


Fig. 18. Phase diagram U-W-C at 1500 °C, ref. 3)

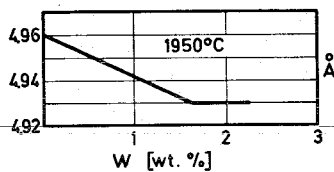


Fig. 19. Lattice parameter of the solid solution (U, W)C, ref. 26).

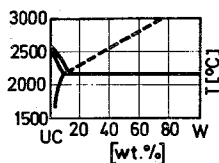


Fig. 20. Quasibinary system UC-W, ref. 27).

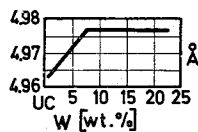


Fig. 21. Lattice parameter of the solid solution (U, W)C, ref. 27).

2.1.15. U-Mn-C

There is a ternary compound $\frac{1}{2}UMnC_2$ 28); (table 1).

2.1.16. U-Tc-C

A ternary phase $UTeC_2$ exists 28).

2.1.17. U-Re-C (fig. 22)

Ref. 3) investigated the three-component system giving a temperature section at 1500 °C (fig. 22). There exists a ternary phase $UReC_2$.

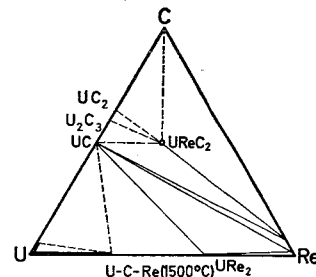


Fig. 22. Phase diagram U-Re-C at 1500 °C, ref. 3).

2.1.18. U-Fe-C (fig. 23)

Ref. 29) finds a eutectic system for the section UC-Fe. In the three-component system 30) (fig. 23) exists a ternary phase $UFeC_2$ (table 1) which melts incongruently at 1615 °C.

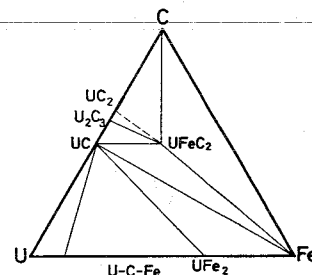


Fig. 23. Phase diagram U-Fe-C, ref. 30).

2.1.19. U-Ru-C

The reaction behaviour is determined by a ternary phase, composition at U_2RuC_2 . At higher Ru-content the following reaction occurs $UC + 3Ru = URu_3C_x + (1-x)C$ 31). The value of x in the three phase field $U_2RuC_2 + URu_3C_x + C$ is approximately one corresponding to the perovskite structure 32).

2.1.20. U-Os-C

Ternary phase U_2OsC_2 31).

2.1.21. U-Co-C

UC and Co are not in equilibrium in the ternary system 33). Ternary phase $UCoC_2$ 34).

2.1.22. U-Rh-C

Ref.²⁸) finds the ternary phase U_2RhC_2 (table 1). With an excess of Rh the phase URh_3 is formed on the section UC-Rh³⁵).

2.1.23. U-Ir-C

A ternary phase U_2IrC_2 exists²⁸). With an excess of Ir the phase UIr_3 is formed on the section UC-Ir³⁵).

2.1.24. U-Ni-C (fig. 24)

Two ternary phases determine the equilibria³⁶): $UNiC_2$ (stable at $T < 1400^\circ C$), U_2NiC_3 (stable at $T < 1800^\circ C$). The solubility of Ni in UC is 1000 ± 300 ppm, in U_2C_3 it is 300 ± 200 ppm at $1400^\circ C$.

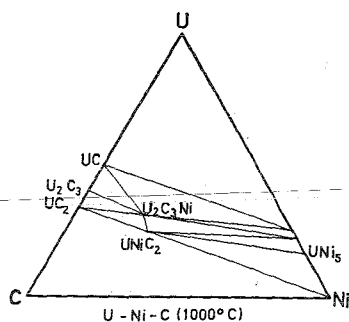


Fig. 24. Phase diagram U-Ni-C at $1000^\circ C$, ref. ³⁶).

2.1.25. U-Pt-C

Ternary phase U_2PtC_2 ³¹).

2.2. U-T₁-T₂-C2.2.1. U-Th-Zr-C (fig. 25)

Fig. 25 shows a section at the composition of 50 at % C²).

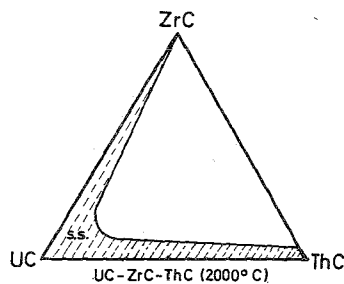


Fig. 25. Solid solution range in the system UC-ThC-ZrC at $2000^\circ C$, ref. ²).

2.2.2. U-Zr-Hf-C (fig. 26)

At $2050^\circ C$ (fig. 31) there is still a small miscibility gap in the concentration section with 50 at % C which will probably be closed at higher temperatures¹⁶).

Accepting the results of¹⁷) in the system UC-HfC, one can conclude that the quasibinary system UC-ZrC-HfC is completely miscible at $2000^\circ C$.

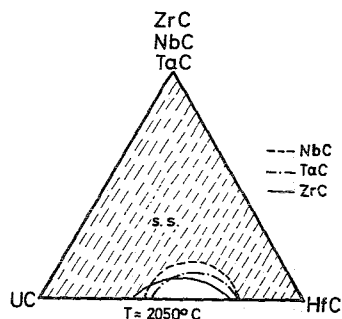


Fig. 26. Solid solution range in the systems UC-HfC-(ZrC, NbC, TaC) at $2050^\circ C$, ref. ¹⁶).

2.2.3. U-Zr-Nb-C (fig. 27)

The quasiternary system UC-ZrC-NbC shows complete miscibility at $2050^\circ C$ ³⁷).

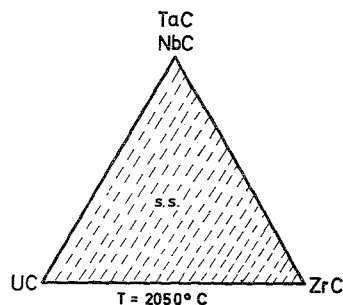


Fig. 27. Solid solution range in the systems UC-ZrC-(NbC, TaC) at $2050^\circ C$, ref. ³⁷).

2.2.4. U-Zr-Ta-C (fig. 27)

Here also there is complete miscibility on the monocarbide section at $2050^\circ C$ ³⁷).

2.2.5. U-Hf-Nb-C (fig. 26)

Fig. 26 shows the monocarbide section with a miscibility gap at $2050^\circ C$ ¹⁶).

2.2.6. U-Hf-Ta-C (fig. 26)

Fig. 26 shows the monocarbide section with a miscibility gap at 2050 °C¹⁶).

2.2.7. U-Nb-Ta-C

The monocarbide section shows complete miscibility at 2050 °C³⁷).

2.2.8. U-Cr-Fe-C

While Fe and Cr are stable in the solid state along with UC, the solid solution Fe-Cr reacts with UC²¹).

2.3. Pu-T-C2.3.1. Pu-Th-C

PuC and ThC are completely miscible³⁸). PuC₂ can be dissolved in monoclinic ThC₂ up to (Th_{0.6}Pu_{0.4})C₂³⁹). Ref. 40) gives a quasibinary section of the system ThC₂-PuC₂. The cubic modifications are completely miscible.

2.3.2. Pu-Zr-C

Arc-molten samples in the section ZrC-PuC, subsequently annealed at 1500 °C, give a single-phase structure up to 24.8 % PuC⁴¹).

2.3.3. Pu-Ta-C

In the system PuC-TaC only a limited solubility could be detected so far⁴¹).

2.3.4. Pu-Mo-C (fig. 28)

Ref.⁴⁰) found two ternary compounds: Pu₄Mo₃C₃, and PuMoC₂ (melting point 2150 °C) transforming to the UMoC₂ structure above 1680 °C.

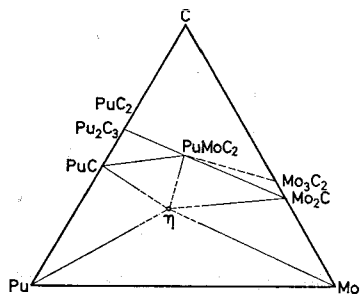


Fig. 28. Tie lines in the system Pu-Mo-C, ref. 40).

2.3.5. Pu-Fe-C (fig. 29)

In addition to PuFeC₂ (isomorphous to UFeC₂) there is still another ternary phase η ³⁰).

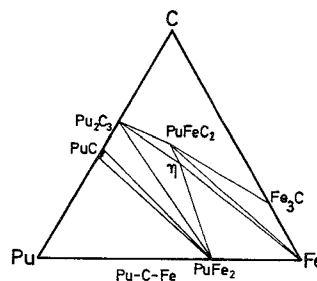


Fig. 29. Phase diagram Pu-Fe-C, ref. 30).

2.4. (U_{1-x}Pu_x)-T-C; $x=0$ to $x=1$ (fig. 30)2.4.1. (U_{1-x}Pu_x)-Th-C

Ref.⁴²) gives a section at 50 at % C in the four-component system Th-U-Pu-C.

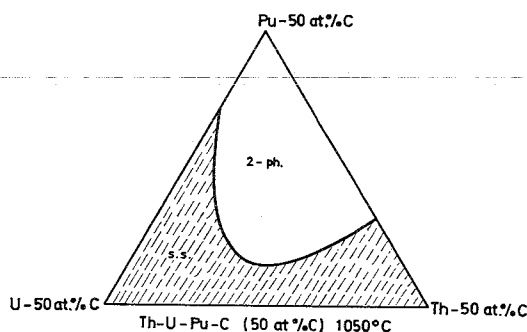


Fig. 30. Quasiternary system ThC-UC-PuC at 1050 °C (at 50 at % C), ref. 42).

2.4.2. (U_{1-x}Pu_x)-Ti-C; $x=0.15$ (fig. 31)

This section in the four-component system at $x=0.15$ essentially agrees with the isothermal section U-Ti-C⁹).

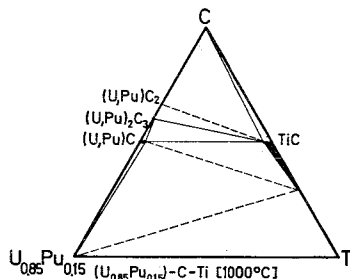


Fig. 31. Phase diagram (U-Pu)-Ti-C at 1000 °C, ref. 8).

2.4.3. $(U_{1-x}Pu_x)\text{-Zr-C}$

In the system U-Pu-Zr-C there is a broad homogeneous region of the mixed phase (U, Pu, Zr)C⁴³. Up to $x=0.15$ the sections in the system U-Zr-C and $(U_{1-x}Pu_x)\text{-Zr-C}$ are similar.

2.4.4. $(U_{1-x}Pu_x)\text{-Mo-C}$; $x=0.15$

Also in this case, the equilibrium conditions are changed only slightly relative to U-Mo-C. Analogous to $UMoC_2$ and $UMoC_{1.7}$ there are the phases $U_{1-x}Pu_xMoC_2$ and $U_{1-x}Pu_xMoC_{1.7}$ according to⁴⁴.

2.4.5. $(U_{1-x}Pu_x)\text{-Fe-C}$

For details see³⁰. $(U_{0.9}Pu_{0.1})\text{C-Fe}$ and $(U_{0.7}Pu_{0.3})\text{C-Fe}$ are eutectic systems.

3. $U\text{-Pu-X-C}$

X = metals or non-metals of the B-groups.

3.1. $U\text{-X-C}$ 3.1.1. $U\text{-Cu-C}$

UC-Cu forms a eutectic system (eutectic at 95 wt % Cu)³³.

3.1.2. $U\text{-Au-C}$

UC + 3. Au form $UAu_3 + C$ at 1000 °C³⁵.

3.1.3. $U\text{-Zn-C}$

At temperatures below 725 °C, UC reacts with Zn forming $UZn_{8.5}$. At higher temperatures UC is in equilibrium with Zn⁴⁵. There exists a zinc-rich ternary carbide with $a=12.71 \text{ \AA}$ ³².

3.1.4. $U\text{-B-C}$ (fig. 32)

The equilibria in the ternary system are determined by the UBC ternary-phase⁴⁶.

3.1.5. $U\text{-Al-C}$

There is no quasibinary equilibrium UC-Al. Two ternary carbides were found as UAl_5C_4 and $U_2Al_3C_3$ ⁴⁷.

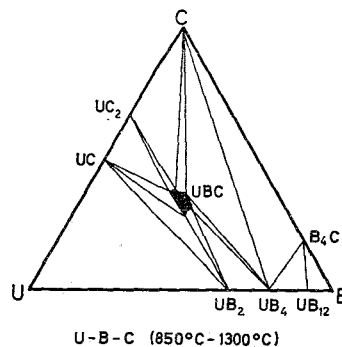


Fig. 32. Phase diagram U-B-C (850–1300 °C), ref. 46).

3.1.6. $U\text{-Si-C}$ (fig. 33)

The system contains the ternary phases $U_3Si_2C_3$ (decomposes at 1750 °C) and $U_{20}Si_{16}C_3$ (decomposes at 1600 °C) (table 1)⁴⁸. Only the U_3Si_2 phase has a homogeneous region in the three-component system.

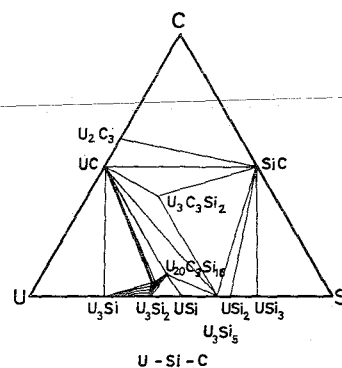


Fig. 33. Phase diagram U-Si-C, ref. 48).

3.1.7. $U\text{-N-C}$

Not treated in this paper; see ref.¹).

3.1.8. $U\text{-P-C}$

UP is practically insoluble in UC, whereas UP dissolves about 5 mole % UC at 1600 °C⁴⁹, fig. 34.

3.1.9. $U\text{-As-C}$

At 1800 °C there is no solubility between the isomorphous compounds UC and UAs⁵⁰, fig. 34.

3.1.10. $U\text{-O-C}$

Not treated in this paper; see ref.¹).

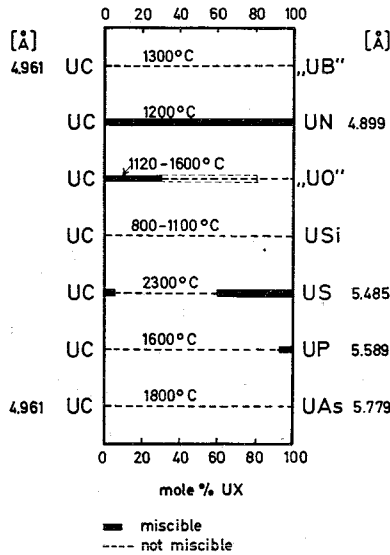


Fig. 34. Solid solution range in the quasibinary systems UC-UX (X=B, N, O, Si, P, S, As).

3.1.11. U-S-C

Ref.⁵¹) investigated the quasibinary system UC-US. At 2300 °C, UC dissolves about 6 mole % of US and US about 30 mole % of UC, fig. 34.

3.2. Pu-X-C

3.2.1. Pu-Si-C (fig. 35)

Ref.⁴⁰) found no ternary compound. The tie lines are given in fig. 35.

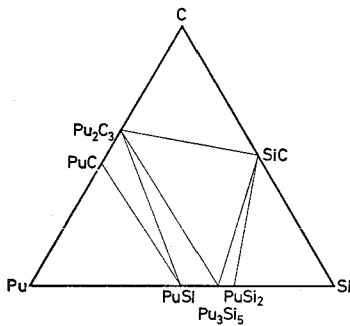


Fig. 35. Tie lines in the system Pu-Si-C, ref. 40).

3.2.2. Pu-N-C

PuC and PuN are completely miscible⁵²). For details see ref.¹).

3.2.3. Pu-O-C (fig. 36)

PuC dissolves about 78 at % of "PuO"⁵³). For details, ref.¹).

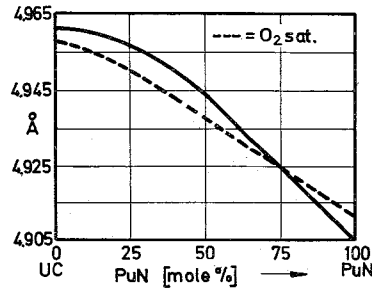


Fig. 36. Lattice parameter in the systems UC-PuN, and U(C, O)-Pu (N, O) (dashed line), ref. 53).

3.3. (U_{1-x}Pu_x)-X-C

3.3.1. (U_{1-x}Pu_x)-N-C

UC-UN, PuC-PuN, and UC-PuN are completely miscible⁵³), i.e. the monocarbide and -nitride section, resp. will be probably completely miscible throughout the four-component system.

3.3.2. (U_{1-x}Pu_x)-O-C

Ref.⁵⁴) gives the values of the lattice parameters for the mixed phase (U_{0.85}Pu_{0.15})C_{1-x}O_x which indicate a solubility of about 50 mole % (U_{0.85}Pu_{0.15})O in (U_{0.85}Pu_{0.15})C (fig. 37).

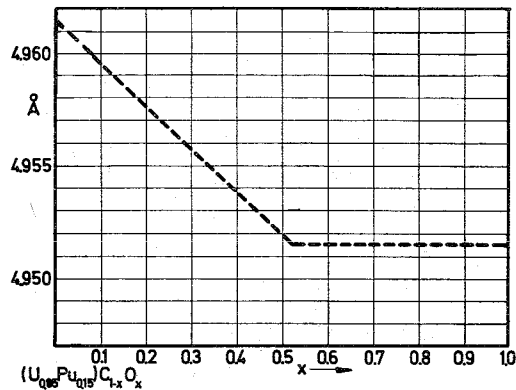


Fig. 37. Lattice parameter of the solid solution (U_{0.85}Pu_{0.15})C_{1-x}O_x, ref. 54).

3.4. U-X₁-X₂-C

3.4.1. U-N-O-C (fig. 38)

Ref.⁵³) indicates the solubility behaviour of the carboxynitrides.

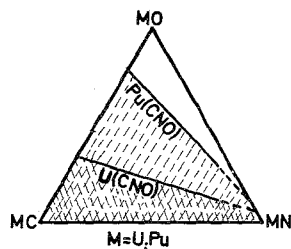


Fig. 38. The range of solid solutions of U(C, N, O) and Pu(C, N, O), ref. ⁵³).

3.5. Pu-X₁-X₂-C3.5.1. Pu-N-O-C (fig. 38)

Fig. 38 shows the carboxynitride mixed crystal range ⁵³).

3.6. U_{1-x}Pu_x-X₁-X₂-C3.6.1. U_{1-x}Pu_x-N-O-C (fig. 39)

The observed phases in the quasibinary system are given ⁵⁵) in fig. 39 for $x=0.1$.

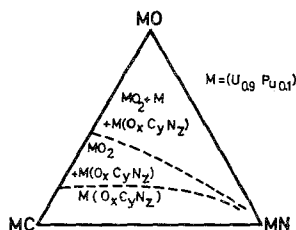


Fig. 39. Phases observed in the quasibinary section MC-MN-MO ($M=U_{0.9}Pu_{0.1}$), ref. ⁵⁵).

4. Multi-component phases in the systemsU-Pu-T-C and U-Pu-X-C

Table 1 lists the known complex carbides containing uranium and plutonium, resp., which can be classified into three groups:

1. The double carbides of uranium and plutonium, resp., with the transition metals of the sixth and seventh groups which are obviously isotype;

2. The isotype double carbides with the iron metals Fe, Co and Ni;
3. The isotype complex carbides with the platinum metals.

Moreover the existence of the so-called carbon-stabilized phases, in particular carbides of the perovskite type are probable. In the case of URu_3 the inclusion of octahedral voids with carbon up to a composition of approximately URu_3C could be proved ³²). This stoichiometry corresponds to the perovskite structure. Further phases, URh_3C_{1-x} and UIr_3C_{1-x} or Pu_3InC_{1-x} and Pu_3GaC_{1-x} , e.g., can be assumed.

B. Thermodynamic data †

The free enthalpies of formation of ternary carbides have not yet been measured directly. However, if a ternary compound exists and the phase diagram of the system is well known, it is possible to calculate the upper and lower limits of the free enthalpy of formation of the ternary carbide, using the tie-lines of the quasibinary equilibria and the free enthalpies of formation of the boundary phases listed in table 3. The values for the free enthalpies of formation of ternary uranium and plutonium carbides, resp., have been calculated where suitable phase diagrams were available. The limits are given in table 4 for room temperature and 1800 °K.

In the case of complete miscibility between two binary carbides with no ternary compounds occurring, the stability of the solid solution was calculated in ¹⁶) from the course of the tie lines in two phase fields of quasiternary systems. The free enthalpies of mixing and the excess functions are listed in table 2.

2.1.3.* U-Gd-C

The change in the free enthalpy of mixing in transforming from tetragonal to cubic $(U, Gd)_2C_2$ solid solutions is

† The thermodynamic symbols are explained in the appendix.

* The numbers correspond to those in part A.

TABLE I
Ternary uranium carbides and plutonium carbides.

System	Carbide	Structure	Lattice parameter (Å)			Ref.
			a	b	c	
U-Pu-T-C	UVC ₂	—	—	—	—	19)
	UCrC ₂	orthorh.	5.42	3.22	10.61	20)
	UMoC ₂	orthorh.	5.625	3.249	10.980	20, 22)
	UMoC _{1.7}	monocl.	5.626	3.238	(11.661 β=109°	24)
	UWC ₂	orthorh.	5.6286	3.2514	10.9740	20, 28)
	U _{0.85} Pu _{0.15} MoC ₂	orthorh.	—	—	—	44)
	U _{0.85} Pu _{0.15} MoC _{1.7}	monocl.	—	—	—	44)
	PuMoC ₂	(T > 1680 °C orthorh.	—	—	—	40)
	Pu ₄ Mo ₃ C ₃	—	—	—	—	40)
	UMnC ₂	orthorh.	5.04	3.172	10.74	28)
	UTeC ₂	orthorh.	5.4	3.22	10.9	28)
	UReC ₂	orthorh.	5.489	3.2229	10.7416	3)
	UFeC ₂	tetr.	4.942	—	7.381	34)
	UCoC ₂	tetr.	4.944	—	7.316	34)
	UNiC ₂	tetr.	4.961	—	7.346	34)
	U ₂ NiC ₃	—	—	—	—	36)
	U ₂ RuC ₂	tetr.	3.45	—	12.52	31)
	* U ₂ OsC ₂	tetr.	3.46	—	12.59	31)
	U ₂ RhC ₂	tetr.	3.466	—	12.512	28)
	U ₂ IrC ₂	tetr.	3.4790	—	12.4780	28)
U ₂ PtC ₂	tetr.	3.52	—	12.54	31)	
PuFeC ₂	tetr.	—	—	—	30)	
η(Pu-Fe-C)	cubic	10.10	—	—	30)	
U-Pu-X-C	UBC	orthorh.	3.591	11.95	3.372	46)
	UAl ₅ C ₄	—	—	—	—	47)
	U ₂ Al ₃ C ₃	—	—	—	—	47)
	U ₃ Si ₂ C ₃	orthorh.	3.598	3.535	18.964	48)
	U ₂₀ Si ₁₆ C ₃	—	—	—	—	48)

* U₂OsC₂ has a homogeneous region with an orthorhombic cell for all other compositions than U₂OsC₂.

$${}^m\Delta G(t \rightarrow c) =$$

$$= -x(1-x)[5330 \pm 960 - (2.29 \pm 0.62)T]$$

cal/mole,

where x denotes the mole fraction of GdC₂ in the solid solution ⁶⁾. The heat of transformation from tetragonal to cubic GdC₂ at 1275 °C is calculated to be ${}^t\Delta H(\text{GdC}_2) = (3070 \pm 440)$ cal/mole.

2.1.7. U-Zr-C (fig. 6)

2.1.8. U-Hf-C (fig. 8)

2.1.10. U-Nb-C (fig. 10)

2.1.11. U-Ta-C (fig. 11)

Refs.^{11, 16, 56)} approximately calculated the free enthalpies of mixing for regular solid solutions of the type (U,Me)C which are defined as

$${}^m\Delta G = {}^{xs}\Delta G + {}^m\Delta G^{id} = a_{\text{UC-MeC}} \cdot x(1-x) + RT[x \ln x + (1-x)\ln(1-x)].$$

The excess function and the heat of mixing are given by

$${}^{xs}\Delta G = {}^m\Delta H = a \cdot x \cdot (1-x).$$

TABLE 2

Free enthalpies of mixing ${}^m\Delta G$ of solid solutions (U, Me)C at 2323 °K.

Compound	a_{UC-MeC} [cal]	${}^{xs}\Delta G$ [cal]	${}^m\Delta G$ [cal]	Ref.
(U _{0.5} , Zr _{0.5})C	6000	+1500	-1700	16, 56)
(U _{0.5} , Hf _{0.5})C	9600	+2400	- 800	16, 56)
(U _{0.5} , Nb _{0.5})C	6800	+1700	-1500	16, 56)
(U _{0.5} , Ta _{0.5})C	8000	+2000	-1200	11, 56)

TABLE 3

Thermodynamic properties of carbides per mole MeC_x.

Compound	C_p^{298} (Cl)	Ref.	S_{298}^0 (Cl)	Ref.	${}^i\Delta H_{298}^0$ (kcal/mole)	Ref.	${}^i\Delta G_{298}^0$ (kcal/mole)	Ref.	${}^i\Delta G_{1800}^0$ (kcal/mole)	Ref.
ThC	—	—	12.0 ^b	57)	-29.6	65)	-29.0 ^c	—	—	—
ThC _{1.93}	13.55	58)	16.37 ^a	58)	-29.7	65)	-30.0	66)	-33.8	66)
UC	12.11	59)	14.28	59)	-23.2	66)	-23.4	66)	-25.5	66)
$\frac{1}{2}$ U ₂ C ₃	12.83 ^a	60)	16.47 ^a	60)	-24.5	68)	-24.6	66)	-26.4	66)
UC _{1.94}	14.52 ^a	60)	16.33 ^a	60)	-20.5	66)	-21.2	66)	-26.4	66)
PuC _{0.87}	12.03	61)	17.33	61)	-10.2	66)	-11.2	66)	-12.2	66)
$\frac{1}{2}$ Pu ₂ C ₃	—	—	20.81	62)	-12.3	62)	-13.9	62)	-17.6	65)
PuC _{2-x}	—	—	22.5	81)	-13.5	81)	>-17 ^b	69)	-17 ^b	69)
TiC	8.08	65)	5.79	65)	-44.1	65)	-43.3 ^c	—	-39.3 ^c	—
ZrC _{0.93}	9.016	65)	7.927	65)	-47.0	65)	-46.2 ^c	—	-42.2 ^c	—
HfC _{0.96}	8.955	65)	9.431	65)	-50.08	65)	-48.6 ^c	—	-43.2 ^c	—
$\frac{1}{2}$ V ₂ C	—	—	—	—	-16.5	65)	-16.1 ^b	—	—	—
VC _{0.88}	7.72	65)	6.61 ^a	65)	-24.5 ^b	65)	-24.0 ^c	—	-20.4 ^c	—
$\frac{1}{2}\beta$ -Nb ₂ C	7.59	65)	7.66	65)	-23.3	65)	-22.8 ^c	—	-20.5 ^c	—
NbC	8.79	65)	8.29	65)	-33.6	65)	-33.1 ^c	—	-31.7 ^c	—
$\frac{1}{2}$ Ta ₂ C	—	—	10.0 ^b	57)	-24.9	65)	-24.7 ^c	—	—	—
TaC	8.764	65)	10.1	65)	-34.1	65)	-33.8 ^c	—	-34.0 ^c	—
$\frac{1}{3}$ Cr ₃ C ₂	7.84	65)	6.81	65)	- 5.5	65)	5.6 ^c	—	- 6.9 ^c	—
$\frac{1}{3}$ Mo ₂ C	—	—	7.87	67)	- 5.5	65)	- 5.4 ^c	—	- 7.2	70)
α -MoC _{1-x}	—	—	—	—	- 3.0	65)	- 3.0 ^b	—	- 6.8	70)
$\frac{1}{2}\alpha$ -W ₂ C	—	—	—	—	- 6.3	65)	- 6.4 ^b	—	—	—
α -WC	8.62 ^b	57)	10.0 ^b	57)	- 9.67	65)	- 9.9 ^c	—	- 8.0 ^d	65)
$\frac{1}{3}$ Mn ₃ C	7.44	63)	7.9	63)	- 1.20	57)	- 1.20 ^c	—	- 1.1	64)
$\frac{1}{3}$ Fe ₃ C	8.44	63)	8.1	63)	+ 1.8	57)	+ 1.45 ^c	—	0	64)
$\frac{1}{3}$ Co ₃ C	—	—	7.6	64)	+ 3.11	64)	+ 3.0 ^c	—	—	—
$\frac{1}{3}$ Ni ₃ C	—	—	8.5 ^b	57)	+ 3.0	57)	+ 2.9 ^c	—	—	—

^a randomization entropy not included; ^b estimated; ^c calculated with ${}^i\Delta H_{298}^0$, C_p and S_{298}^0 ; ^d at 1300 °K.

The quasiternary diagrams UC-HfC-MeC, (U,Hf)C, (U,Nb)C and (U,Ta)C with an equimolar composition. By this method the excess functions become positive. It may be pointed out again that, according to ¹⁷⁾, Ue and HfC are completely miscible at 2000 °C.

The interaction parameters a were determined ¹⁶⁾ from the course of the tie lines in the two phase fields and the position of the plait points. Table 2 shows the result obtained at 2323 °K for the solid solutions (U,Zr)C,

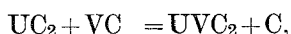
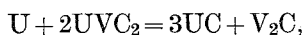
(U,Hf)C, (U,Nb)C and (U,Ta)C with an equimolar composition. By this method the excess functions become positive. It may be pointed out again that, according to ¹⁷⁾, Ue and HfC are completely miscible at 2000 °C.

2.1.9. U-V-C (fig. 9)

From the proposed phase diagram ¹⁹⁾ it is possible to calculate the upper and lower

limits of the free enthalpy of formation of UVC_2 using the thermodynamic data of the binary carbides.

With the following reactions

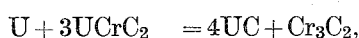
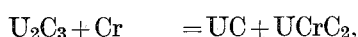


we obtain:

$$\begin{aligned} \frac{3}{2} \Delta G^0(UC) + \frac{1}{2} \Delta G^0(V_2C) &< \Delta G^0(UVC_2) < \\ &< \Delta G^0(UC_2) + \Delta G^0(VC), \\ -51200 \text{ cal/mole} &< \Delta G^0_{298}(UVC_2) < \\ &< -45200 \text{ cal/mole,} \\ \Delta G^0_{1800}(UVC_2) &< -46800 \text{ cal/mole.} \end{aligned}$$

2.1.12. U-Cr-C (fig. 12)

From the phase diagram ²¹⁾ we can infer that the following reactions occur:

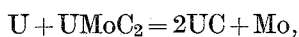


and therefore

$$\begin{aligned} \frac{4}{3} \Delta G^0(UC) + \frac{1}{3} \Delta G^0(Cr_3C_2) &< \Delta G^0(UCrC_2) < \\ &< \Delta G^0(U_2C_3) - \Delta G^0(UC), \\ -36800 \text{ cal/mole} &< \Delta G^0_{298}(UCrC_2) < \\ &< -25800 \text{ cal/mole,} \\ -40900 \text{ cal/mole} &< \Delta G^0_{1800}(UCrC_2) < \\ &< -27300 \text{ cal/mole.} \end{aligned}$$

2.1.13. U-Mo-C (fig. 14)

Neglecting solubility effects in the U-rich region, the upper and lower limits of the free enthalpy of formation of $UMoC_2$ were fixed with the aid of the following reactions ^{56, 71)}:

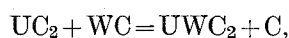
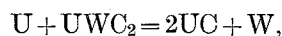


This leads to the inequalities:

$$\begin{aligned} 2 \Delta G^0(UC) &< \Delta G^0(UMoC_2) < \Delta G^0(UC) + \\ &+ \Delta G^0(Mo_2C). \\ -46800 \text{ cal/mole} &< \Delta G^0_{298}(UMoC_2) < \\ &< -34600 \text{ cal/mole,} \\ -51000 \text{ cal/mole} &< \Delta G^0_{1800}(UMoC_2) < \\ &< -39900 \text{ cal/mole.} \end{aligned}$$

2.1.14. U-W-C (fig. 18)

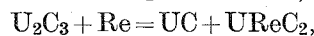
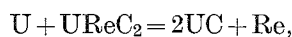
With a similar calculation for UWC_2 we obtain ^{56, 71)}:



$$\begin{aligned} 2 \Delta G^0(UC) &< \Delta G^0(UWC_2) < \Delta G^0(UC_2) + \\ &+ \Delta G^0(WC), \\ -46800 \text{ cal/mole} &< \Delta G^0_{298}(UWC_2) < \\ &< -31100 \text{ cal/mole,} \\ -51000 \text{ cal/mole} &< \Delta G^0_{1800}(UWC_2) < \\ &< -34400 \text{ cal/mole.} \end{aligned}$$

2.1.17. U-Re-C (fig. 22)

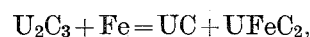
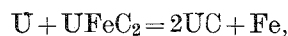
From the phase diagram ³⁾ the following reactions are available:



$$\begin{aligned} 2 \Delta G^0(UC) &< \Delta G^0(UReC_2) < \Delta G^0(U_2C_3) - \\ &- \Delta G^0(UC), \\ -46800 \text{ cal/mole} &< \Delta G^0_{298}(UReC_2) < \\ &< -25800 \text{ cal/mole,} \\ -51000 \text{ cal/mole} &< \Delta G^0_{1800}(UReC_2) < \\ &< -27300 \text{ cal/mole.} \end{aligned}$$

2.1.18. U-Fe-C (fig. 23)

Based on the phase diagram ³⁰⁾ the limits of the free enthalpy of formation of $UFeC_2$ can be stated to be:



$$\begin{aligned} 2 \Delta G^0(UC) &< \Delta G^0(UFeC_2) < \Delta G^0(U_2C_3) - \\ &- \Delta G^0(UC), \\ -46800 \text{ cal/mole} &< \Delta G^0_{298}(UFeC_2) < \\ &< -25800 \text{ cal/mole,} \\ -51000 \text{ cal/mole} &< \Delta G^0_{1800}(UFeC_2) < \\ &< -27300 \text{ cal/mole.} \end{aligned}$$

2.1.24. U-Ni-C (fig. 24)

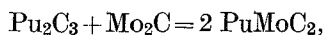
The upper limit of the free enthalpy of

formation of the two existing phases ³⁶⁾ was estimated by the equations:

$$\begin{aligned} \text{UC}_2 + \text{Ni} &= \text{UNiC}_2, \\ {}^f\Delta G^0(\text{UNiC}_2) &< {}^f\Delta G^0(\text{UC}_2), \\ {}^f\Delta G^0_{298}(\text{UNiC}_2) &< -21200 \text{ cal/mole}, \\ {}^f\Delta G^0_{1800}(\text{UNiC}_2) &< -26400 \text{ cal/mole}; \\ \text{U}_2\text{C}_3 + \text{Ni} &= \text{U}_2\text{NiC}_3, \\ {}^f\Delta G^0(\text{U}_2\text{NiC}_3) &< {}^f\Delta G^0(\text{U}_2\text{C}_3) \\ {}^f\Delta G^0_{298}(\text{U}_2\text{NiC}_3) &< -49200 \text{ cal/mole}, \\ {}^f\Delta G^0_{1800}(\text{U}_2\text{NiC}_3) &< -52800 \text{ cal/mole}. \end{aligned}$$

2.3.4. Pu-Mo-C (fig. 28)

From the phase diagram ⁴⁰⁾ only the upper limit of the free enthalpy of formation of PuMoC₂ can be calculated. Since

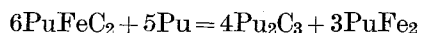


it follows:

$$\begin{aligned} {}^f\Delta G^0(\text{PuMoC}_2) &< \frac{1}{2} {}^f\Delta G^0(\text{Pu}_2\text{C}_3) + \frac{1}{2} {}^f\Delta G^0(\text{Mo}_2\text{C}), \\ {}^f\Delta G^0_{298}(\text{PuMoC}_2) &< -19300 \text{ cal/mole}, \\ {}^f\Delta G^0_{1800}(\text{PuMoC}_2) &< -24800 \text{ cal/mole}. \end{aligned}$$

2.3.5. Pu-Fe-C (fig. 29)

Because of the existence of a second (η) phase only the lower limit of the free enthalpy of formation of PuFeC₂ can be given from the phase diagram ³⁰⁾. Since



and

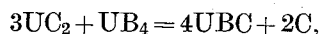
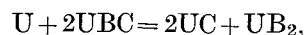
$${}^f\Delta G^0_{298}(\text{PuFe}_2) = -3700 \text{ cal/mole } ^{72)},$$

it follows:

$$\begin{aligned} \frac{2}{3} {}^f\Delta G^0(\text{Pu}_2\text{C}_3) + \frac{1}{2} {}^f\Delta G^0(\text{PuFe}_2) &< {}^f\Delta G^0(\text{PuFeC}_2), \\ {}^f\Delta G^0_{298}(\text{PuFeC}_2) &> -20300 \text{ cal/mole}. \end{aligned}$$

3.1.4. U-B-C (fig. 32)

The following reactions can be used to determine the limits of the free enthalpy of formation of UBC from the phase diagram ⁴⁶⁾:



$$\begin{aligned} {}^f\Delta G^0(\text{UC}) + \frac{1}{2} {}^f\Delta G^0(\text{UB}_2) &< {}^f\Delta G^0(\text{UBC}) < \\ &< \frac{3}{4} {}^f\Delta G^0(\text{UC}_2) + \frac{1}{4} {}^f\Delta G^0(\text{UB}_4). \end{aligned}$$

With the free enthalpies of formation ⁶⁸⁾ of UB₂ and UB₄:

$${}^f\Delta G^0_{298}(\text{UB}_2) = -35600 \text{ cal/mole}$$

and

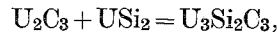
$${}^f\Delta G^0_{298}(\text{UB}_4) = -58500 \text{ cal/mole}$$

we get:

$$\begin{aligned} -41200 \text{ cal/mole} &< {}^f\Delta G^0_{298}(\text{UBC}) < \\ &< -30500 \text{ cal/mole}. \end{aligned}$$

3.1.6. U-Si-C (fig. 33)

From the phase diagram ⁴⁸⁾ the following reactions are suitable for estimating the free enthalpy of formation of the ternary compound U₃Si₂C₃:



$$\begin{aligned} 3 {}^f\Delta G^0(\text{UC}) + \frac{2}{5} {}^f\Delta G^0(\text{U}_3\text{Si}_5) &< {}^f\Delta G^0(\text{U}_3\text{Si}_2\text{C}_3) < \\ &< {}^f\Delta G^0(\text{U}_2\text{C}_3) + {}^f\Delta G^0(\text{USi}_2). \end{aligned}$$

With the free enthalpies of formation for the U-Si-compounds ⁷²⁾:

$${}^f\Delta G^0_{298}(\text{U}_3\text{Si}_5) = -83700 \text{ cal/mole},$$

$${}^f\Delta G^0_{1773}(\text{U}_3\text{Si}_5) = -70250 \text{ cal/mole},$$

$${}^f\Delta G^0_{298}(\text{USi}_2) = -30600 \text{ cal/mole},$$

$${}^f\Delta G^0_{1773}(\text{USi}_2) = -25300 \text{ cal/mole}$$

we obtain:

$$\begin{aligned} -103700 \text{ cal/mole} &< {}^f\Delta G^0_{298}(\text{U}_3\text{Si}_2\text{C}_3) < \\ &< -79800 \text{ cal/mole}, \\ -104600 \text{ cal/mole} &< {}^f\Delta G^0_{1800}(\text{U}_3\text{Si}_2\text{C}_3) < \\ &< -78100 \text{ cal/mole}. \end{aligned}$$

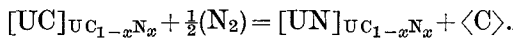
3.1.7. U-N-C

UC and UN form a continuous series of solid solutions ⁷³⁾. The stable composition range is dependent on temperature and nitrogen pres-

sure. Assuming a regular behaviour of the mixed crystal $UC_{1-x}N_x$, it was proposed by ⁷⁴⁾ to determine the free enthalpy of formation of $UC_{1-x}N_x$,

$$\begin{aligned} {}^f\Delta G^0\langle UC_{1-x}N_x \rangle &= x {}^f\Delta G^0\langle UN \rangle + \\ &+ (1-x) {}^f\Delta G^0\langle UC \rangle + RT[x \ln x + \\ &+ (1-x) \ln(1-x)] + 6Wx(1-x), \end{aligned}$$

from the equilibrium



This leads to the thermochemical equation

$$\begin{aligned} \frac{1}{2} RT \ln p(N_2) &= {}^f\Delta G^0\langle UN \rangle - \\ &- {}^f\Delta G^0\langle UC \rangle + RT \ln \left\{ \frac{x}{(1-x)} \right\} + 6W(1-2x). \end{aligned}$$

The interaction parameter $a = 6W$ of the excess function ${}^{xs}\Delta G = 6Wx(1-x)$ was recalculated with the experimental results of ⁷⁵⁾ who measured the pressure dependence on composition at various temperatures and determined the composition of the solid solution by chemical analysis. Taking the free enthalpies of formation for UC from ⁶⁶⁾ and for UN from ⁶⁸⁾, an approximate value of $a = -(3600 \pm 1800)$ cal/mole results. A dependence on composition and temperature of the interaction parameter cannot be shown with the results of ⁷⁵⁾ because W is calculated from a difference of three terms of the same order and the error in thermochemical data of UN and UC increases at higher temperatures.

In fig. 40 the free enthalpy of formation of the ideal (a) and regular (b) solid solution is plotted vs concentration. It passes a minimum which shifts to the UC-rich region with increasing temperatures.

Other topics of the system U-N-C will be dealt with in ¹⁾.

3.1.10. U-O-C

The system U-O-C is treated in detail in ¹⁾. Ref.⁷⁷⁾ reports an upper limit of solubility of 25 mole % UO in UC, refs.^{55, 76)} quote 35 mole %, whereas refs.⁷⁸⁻⁸⁰⁾ find approximately 80 mole %. Provided that the solubility of 80 mole % UO in UC is valid, ref.⁷⁸⁾ determined the excess free enthalpy of mixing of the solid

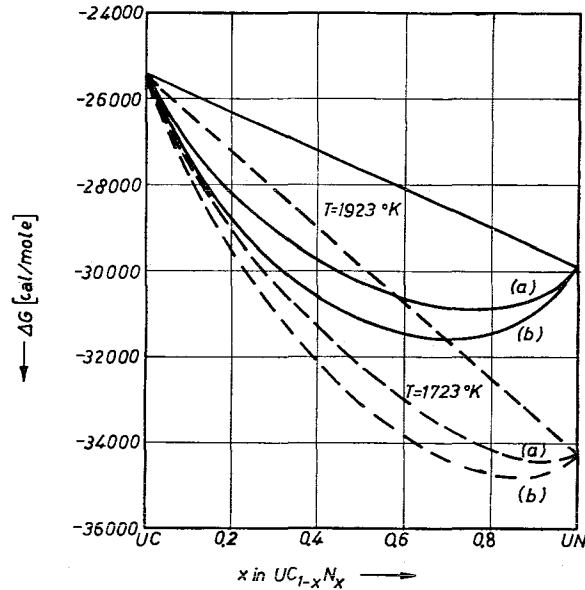


Fig. 40. Free enthalpy of formation for the solid solution $UC_{1-x}N_x$ at various temperatures. (a): ideal solution ${}^f\Delta G^{id}\langle UC_{1-x}N_x \rangle =$

$$= x \cdot {}^f\Delta G^0\langle UN \rangle + (1-x) \cdot {}^f\Delta G^0\langle UC \rangle + {}^m\Delta G^{id};$$

(b): regular solution ${}^f\Delta G^{reg}\langle UC_{1-x}N_x \rangle =$

$$= x \cdot {}^f\Delta G^0\langle UN \rangle + (1-x) \cdot {}^f\Delta G^0\langle UC \rangle + {}^m\Delta G^{id} + {}^{xs}\Delta G.$$

solution $UC_{1-x}O_x$ from electromotive force measurements. However, it seems to be probable that the limit of solubility of UO in UC is about 35 mole %.

4. Free enthalpies of multi-component phases in systems U-Pu-T-C and U-Pu-X-C

The lower and upper limits of the free enthalpies of formation for ternary carbides are compiled in table 4. The intervals would be reduced for some carbides by completion of the phase diagrams and by better knowledge of thermodynamic data for the intermetallic compounds.

Concluding remarks

It can be assumed, as has been shown for various cases in section A, that a mixed crystal phase $(U_{1-x}Pu_x)C$ ($0 < x < 0.2$) plays a similar role with respect to the constitution in multi-component systems as does pure UC. In addition, many results of multi-component

TABLE 4

Free enthalpies of formation of ternary uranium and plutonium carbides.

Compound	${}^f\Delta G_{298}^0$ [cal/mole]		${}^f\Delta G_{1800}^0$ [cal/mole]	
	lower limit	upper limit	lower limit	upper limit
UVC ₂	-51200	-45200	-	-46800
UCrC ₂	-36800	-25800	-40900	-27300
UMoC ₂	-46800	-34600	-51000	-39900
UWC ₂	-46800	-31100	-51000	-34400
UReC ₂	-46800	-25800	-51000	-27300
UFeC ₂	-46800	-25800	-51000	-27300
UNiC ₂	-	-21200	-	-26400
U ₂ NiC ₃	-	-49200	-	-52800
UBC	-41200	-30500	-	-
U ₃ Si ₂ C ₃	-103700	-79800	-104600	-78100
PuMoC ₂	-	-19300	-	-24800
PuFeC ₂	-20300	-	-	-

systems containing uranium carbide will apply to plutonium carbide bearing systems similarly.

In a number of cases it has been shown that it is often difficult to harmonize the investigations by different authors, especially in the field of constitution. This is frequently due to the fact that the reaction rates in high-melting carbide systems are very low and an equilibrium state has not yet been reached or that low oxygen or nitrogen contents change the equilibrium conditions. Uncertainties of this kind naturally influence the estimation of thermodynamic data.

Moreover, it can be seen that the estimated limits of the free enthalpies for the ternary compounds shift to more negative values with rising temperature due to the increasing stability of the binary uranium and plutonium carbides, resp.

Provided the phase diagrams of ternary uranium and plutonium carbides are similar, it can be inferred from the thermochemical data of "PuC" and Pu₂C₃ that the ternary plutonium carbides are less stable than the corresponding uranium phases.

Appendix

COMMONLY USED SYMBOLS, INTEGRAL QUANTITIES

$${}^f\Delta G_T^0 = {}^f\Delta H_T^0 - T \cdot {}^f\Delta S_T^0$$

is the free enthalpy of formation at the standard state and the temperature specified;

$${}^m\Delta G^{\text{id}} = -T \cdot {}^m\Delta S^{\text{id}} = RT(x_1 \ln x_1 + x_2 \ln x_2)$$

is the free enthalpy of mixing for an *ideal* solution;

$${}^m\Delta G = {}^{xs}\Delta G + {}^m\Delta G^{\text{id}}$$

is the free enthalpy of mixing for a *regular* solution;

${}^{xs}\Delta G$ is the excess free enthalpy of mixing for a *regular* or *real* solution;

${}^m\Delta H$ is the enthalpy of mixing (equal to ${}^{xs}\Delta G$ for a *regular* solution);

${}^t\Delta H$ is the enthalpy of transformation.

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