Stabilities of Ternary Carbides $UWC_{1.75}$ and UWC_2

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ABSTRACT

The methane-hydrogen gas equilibration technique has been used to measure the chemical potential of carbon associated with two three-phase fields of the system U-W-C in the temperature range 973 to 1173 K. By combining the values of the chemical potential of carbon in the three-phase fields UC + W + $UWC_{1.75}$ and UC + $UWC_{1.75}$ + UWC_2 obtained in this study with the data on the Gibbs energy of formation of UC available in the literature, expressions for the Gibbs energies of formation of the two ternary carbides were derived:

$\Delta_f G^\circ_{\langle UWC_{1.75}\rangle} = -131,600 - 30.0\ T\ (\pm 8000)$ J mol^{-1}

$\Delta_f G^\circ_{\langle UWC_2\rangle} = -144,800 - 32.0\ T\ (\pm 10.000)$ J mol^{-1}

Although estimates of Gibbs energies of formation of the two ternary carbides $UWC_{1.75}$ and UWC_2 have been reported, there have been no previous experimental determinations of thermodynamic properties of these compounds.

1. INTRODUCTION

Chemical thermodynamic data on the binary, ternary and multicomponent carbides of relevance to nuclear technology are being generated at the Indira Gandhi Centre for Atomic Research, Kalpakkam /1-3/. Recently, the Gibbs energies of formation of the ternary compounds in the system U-Mo-C were determined /4/. Neither the carbon potentials over the three-phase fields nor the Gibbs energies of the ternary compounds in the system U-W-C have been experimentally determined so far. The present work is a part of systematic studies on the ternary systems U-M-C (M = Mo, W, Cr (Group VIB)).

Holleck /5/ proposed an isothermal section of the ternary phase diagram at 1773 K for the system U-W-C, with two ternary compounds, $UWC_{1.75}$ and UWC_2. Recently, Behrens and Jeitschko /6/ identified a new ternary compound UW_4C_4. They proposed a ternary phase diagram at 1173 K for the system U-W-C, in which W_2C is shown to coexist with WC and UW_4C_4, and UC_2 is shown to be in equilibrium with UWC_2 and UC. It is evident from the phase diagrams of the binary systems W-C and U-C that the compounds W_2C and UC_2 are metastable at 1173 K. A modified phase diagram at 1173 K of the system U-W-C, shown in Fig. 1, incorporates the essential ternary phase relations suggested in references /5/, /6/ and /7/ and is consistent with the binary data /8/.

Ugajin *et al.* /9/ made an estimate of the Gibbs energies of formation of the ternary carbides $UWC_{1.75}$ and UWC_2 in the temperature range 298 - 2400 K based on the ternary phase diagram. Their estimates have an uncertainty of at least ±10%. The purpose of the present study was to obtain more accurate data on the Gibbs energies of formation of the two ternary carbides. The carbon potentials in the three-phase fields: a) UC + $UWC_{1.75}$ + UWC_2 and b) $UWC_{1.75}$ + UC + W were measured by using a methane-hydrogen gas equilibration technique in the temperature range 973 to 1173 K. The standard Gibbs energies of formation of the two ternary carbides were determined by combining the measured carbon potentials with standard Gibbs energy of formation of UC reported in the literature /10/.

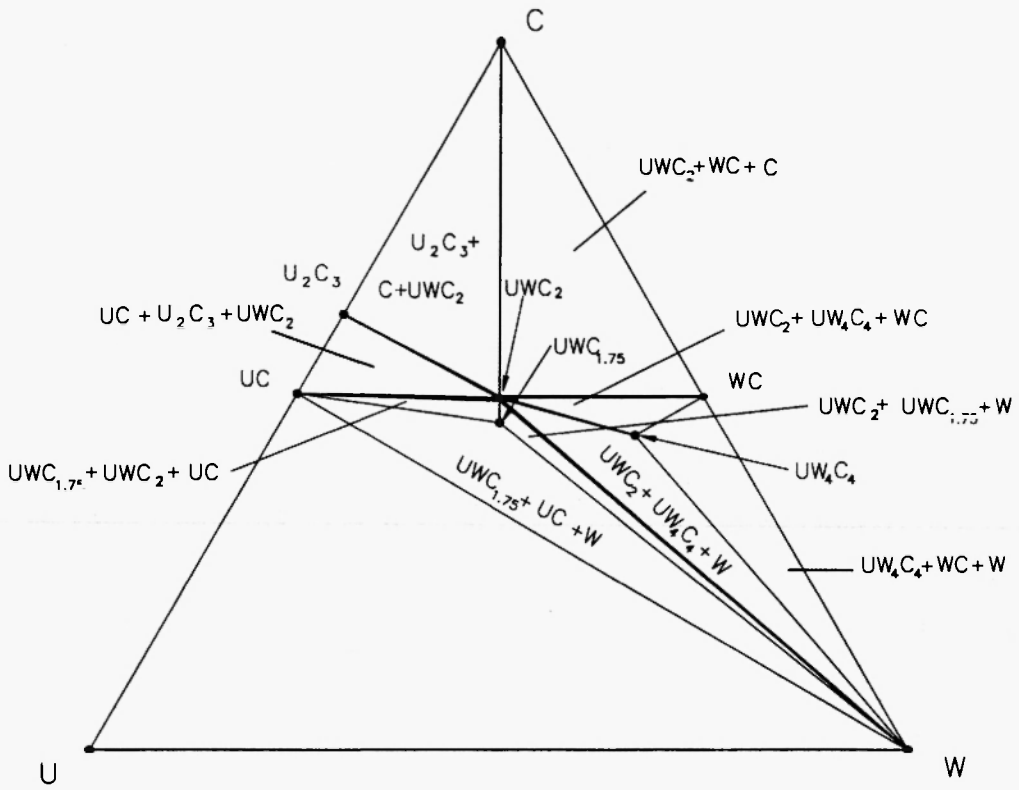

Fig. 1: Modified isothermal section of the phase diagram for the system U-W-C at 1173 K.

2. EXPERIMENTAL DETAILS

2.1. Starting materials

Tungsten (99.9% pure) was obtained from Aldrich Chemical Company, USA, in the form of powder with an average particle size of 12 μm. Uranium was supplied by Atomic Fuels Division, Bhabha Atomic Research Centre, India. Spectroscopic grade graphite was obtained from Leco Corporation, USA.

2.2. Preparation of the three-phase mixtures

The tungsten powder was stored in a glove box filled with argon gas. The uranium metal which was supplied in the form of discs of 15 mm diameter and 3.5 mm thickness was degreased in CCl_4 and cleaned in concentrated nitric acid and water. To prevent surface oxidation, the cleaned metal was stored in acetone for a few minutes until it was used. The graphite was broken into chips and degassed at 473 K at a pressure of 1 Pa for 4 h. The cooled chips were used within 10 minutes for arc melting.

The three-phase mixtures employed in this study were prepared by arc melting the elements in a triarc furnace supplied by Centorr Associates Inc., U.S.A. Mixtures of U + W + C of desired stoichiometry were melted by using a DC arc generated between a nonconsumable, thoriated tungsten cathode and a water cooled copper anode. The melting was done under argon containing about 4 ppm each of oxygen and moisture (IOLAR-2 grade argon gas supplied by Indian Oxygen Limited) at a pressure of 1-10 Pa. To remove the residual oxygen in the arcing chamber, zirconium metal sponge was melted before melting the alloy components. Homogenisation was achieved by repeated melting. These buttons were then annealed at 1873 K for 60 h in a tungsten wire resistance furnace at 10^{-4} Pa. The temperature of the furnace was controlled within ± 5 K by using a PID (Proportional Integral Derivative) controller. The alloys were characterised by chemical analysis for oxygen, carbon, tungsten and uranium. The constituent phases were identified by XRD. Concentration of carbon in the ternary alloys was determined by combustion in oxygen. Oxygen concentration

Table 1
Composition of the ternary alloys used in this study

Alloy composition				Phases identified in XRD
U (wt%)	W (wt %)	C (wt %)	O (ppm)	
53.60	41.40	4.97	500	UC, UWC_2 , $UWC_{1.75}$
34.80	63.80	1.30	500	UC, W, $UWC_{1.75}$

in the three-phase mixtures was measured by inert gas fusion technique using an oxygen analyser supplied by Leco Corporation Inc., U.S.A. Elemental assay obtained from the above analyses along with the phases identified by XRD are shown in Table 1.

To obtain the three-phase mixture UC + $UWC_{1.75}$ + UWC_2, the elements U, W and C were arc melted in the molar ratio 1 : 0.9 : 1.7. The three-phase mixture UC + $UWC_{1.75}$ + W was prepared by arc melting pure W metal powder with an alloy containing 32.5 at% U, 32.5 at% W and 35 at% C. Reflections pertaining to the ternary carbide UWC_2 were not detected in the XRD pattern of the latter alloy even in the as-melted condition.

2.3. Experimental procedure

The alloys used in this study are susceptible to oxidation and hydrolysis. Hence these samples were handled in a glove box filled with high purity argon gas. The details of the glove box system, the experimental assembly and procedure have been reported in detail elsewhere /2,3/. To generate the equilibrium methane pressure above the alloy sample, high purity hydrogen was allowed to react with the sample at the desired temperature for about 24 h. The furnace temperature was controlled within ± 2 K using a PID controller. The pressure of the methane-hydrogen gas mixture in the reaction chamber was maintained constant at 0.1 MPa. To minimise thermal segregation in the gas mixture, the gas phase over the carbide was continuously recirculated. A hermetically sealed circulating pump (supplied by Metal Bellows Corporation, U.S.A.) which had a flow rate varying from 8.3×10^{-6} to 1.7×10^{-5} m^3/s, was used for this purpose.

Quantitative determination of the methane in the gas samples was carried out by using a flame ionization detector (supplied by Gow Mac, U.S.A.). Equilibrium was assumed to have been attained when the methane concentration in the gas phase remained constant for more than 10 h. The equilibrium was disturbed subsequently by flushing hydrogen through the reaction tube. The methane concentration was once again allowed to build up and reach a constant value. In all the measurements the first measurement of CH_4 concentration agreed with the second within ± 10%, suggesting that equilibrium between the gas and condensed phases was attained.

2.4. Errors in measurement

The methane-hydrogen equilibration technique employed in this study was validated in an earlier study /4/. A detailed analysis of the errors associated with the experimental technique has been described in an earlier paper /2/. The overall error involved in the measurement of the chemical potential of carbon is estimated to be ± 2 kJ mol^{-1} based on studies on binary carbides.

3. RESULTS AND DISCUSSION

3.1. Gibbs energy of formation of $UWC_{1.75}$

The measured values of the chemical potential of carbon in the phase field UC + W + $UWC_{1.75}$ relative to graphite as the standard state is shown in Fig. 2. The chemical potential of carbon is calculated from the composition of the gas at equilibrium using the expression:

$$\Delta\mu_C = RT \ln a_C = \Delta_f G^\circ (CH_4) + RT \ln \frac{p_{CH_4}}{p_{H_2}^2} \quad (1)$$

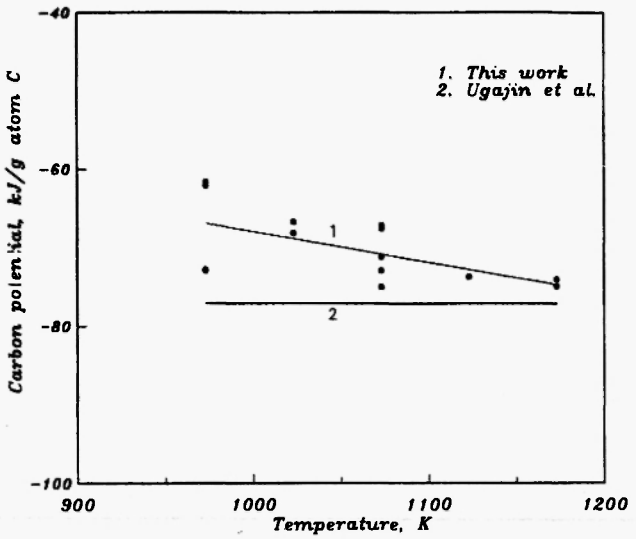

Fig. 2: Temperature dependence of the carbon potential in the three-phase field UC + $UWC_{1.75}$ + W.

Linear least-squares regression analysis of the data gives the expression:

$$\Delta\mu_C = -28,750 - 39.0\ T\ (\pm 7000)\ J\ mol^{-1} \quad (2)$$

where the uncertainty represents twice the random error estimate. The larger spread of results obtained in this study reflects difficulties encountered in the study of equilibrium involving three solid phases with high melting points. In view of the uncertainty in chemical potential and the narrow temperature range in this study reliable information on partial enthalpy and entropy of carbon in the three-phase field cannot be obtained. The chemical potential of carbon in the three-phase field is established by the reaction:

$$\langle UC\rangle + \langle W\rangle + 0.75\ C = \langle UWC_{1.75}\rangle \quad (3)$$

In view of the limited solubility of W in UC, and the limited solubilities of U and C in tungsten /11/ in the temperature range 973 to 1173 K, the activities of UC and W may be assumed to be unity. By combining the carbon potential data obtained in this study with the Gibbs energy of formation of UC reported in the literature /10/, the Gibbs energy of formation of $UWC_{1.75}$ from elements in the temperature range 973 to 1173 K can be calculated as:

$$\Delta_f G^\circ\langle UWC_{1.75}\rangle = -131,600 - 30.0\ T\ (\pm 8000)\ J\ mol^{-1} \quad (4)$$

Ugajin *et al.* /9/ estimated the standard Gibbs energy of formation of this compound from the ternary phase diagram in the temperature range 298 to 2400 K as:

$$\Delta_f G^\circ\langle UWC_{1.75}\rangle = -166,523 - 2.9\ T\ J\ mol^{-1} \quad (5)$$

The uncertainty in their estimate is at least ± 10%, which corresponds to a value of ± 29000 J mol^{-1} at 1073 K. The value of the Gibbs energy of formation of $UWC_{1.75}$ at 1073 K obtained in this study is ~6000 J mol^{-1} more positive than the estimate of Ugajin *et al.* /9/. In view of the large uncertainty in the values estimated by these authors, the Gibbs energy of formation obtained in this study is considered to be more accurate.

3.2. Gibbs energy of formation of UWC_2

The temperature dependence of the chemical potential of carbon in the three-phase field UC + $UWC_{1.75}$ + UWC_2 obtained from the results of this study is shown in Fig. 3. Linear least-squares regression analysis of the data in the temperature range 973 to 1173 K gives the expression

$$\Delta\mu_C = -52,500 - 7.50\ T\ (\pm 8500)\ J\ mol^{-1} \quad (6)$$

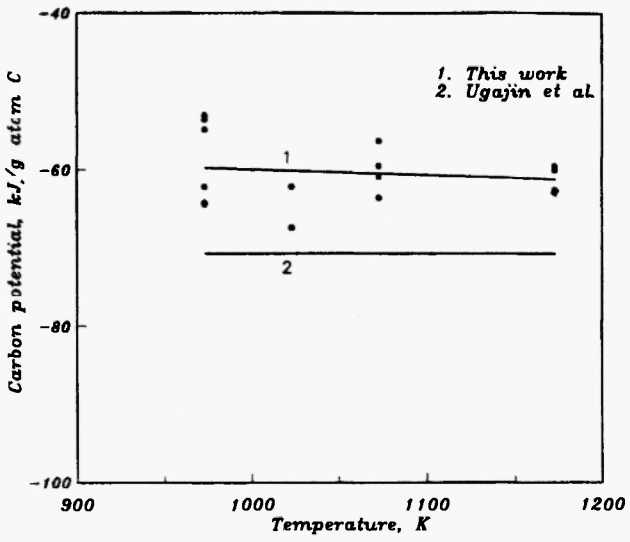

Fig. 3: Temperature dependence of the carbon potential in the three-phase field UC + $UWC_{1.75}$ + UWC_2.

Table 2
Measured values of the carbon potentials in the system U-W-C relative to graphite as the standard state

Condensed phases	Temperature (K)	Time* (h)	$p_{CH_4}/\ p^2_{H_2}$	$\Delta\mu_C$ (J / mol)
$UC + UWC_{1.75} + W$	973	66	1.8694×10^{-5}	-72, 714
		66	1.8611×10^{-5}	-72, 836
		24	7.4968×10^{-5}	-61, 565
		24	7.0808×10^{-5}	-62, 027
	1023	24	3.6105×10^{-5}	-66, 652
		24	3.0589×10^{-5}	-68, 062
	1073	18	2.9740×10^{-5}	-67, 558
		18	3.1367×10^{-5}	-67, 083
		66	1.2943×10^{-5}	-74, 980
		19	1.9980×10^{-5}	-71, 107
		19	1.6479×10^{-5}	-72, 826
	1123	24	1.4393×10^{-5}	-73, 592
		24	1.4357×10^{-5}	-73, 615
	1173	24	1.3261×10^{-5}	-73, 949
		24	1.9664×10^{-5}	-74, 848
$UC + UWC_{1.75} + UWC_2$	973	20	2.1517×10^{-4}	-53, 036
		24	1.7160×10^{-4}	-54, 867
		18	6.9861×10^{-5}	-62, 136
		24	5.3180×10^{-5}	-64, 343
		22	2.0045×10^{-4}	-53, 609
		24	5.4360×10^{-5}	-64, 174
	1023	23	6.1345×10^{-5}	-62, 144
		24	3.3192×10^{-5}	-67, 367
	1073	24	1.0431×10^{-4}	-56, 364
		21	7.3169×10^{-5}	-59, 527
		21	6.2823×10^{-5}	-60, 887
		18	4.6564×10^{-5}	-63, 559
	1173	20	5.5257×10^{-5}	-60, 032
		24	5.8318×10^{-5}	-59, 506
		24	4.2553×10^{-5}	-62, 579

* Equilibration time

The carbon potential in this three-phase field is established by the reaction:

$$\langle UWC_{1.75}\rangle + 0.25\ C = \langle UWC_2\rangle \qquad (7)$$

Since the carbon potential is defined between two ternary phases with identical values for U/W ratio (equation (7)), the chemical potential of carbon in the three-phase fields $UC + UWC_{1.75} + UWC_2$ and $W + UWC_{1.75} + UWC_2$ which share the two ternary carbide phases would be identical.

By combining the Gibbs energy of formation of $UWC_{1.75}$ given by the equation (4) with the measured values of the chemical potential of carbon in the three-phase field $UC + UWC_{1.75} + UWC_2$, the Gibbs energy of formation of UWC_2 from elements is obtained:

$$\Delta_f G^\circ \langle UWC_2\rangle = -144,800 - 32.0\ T\ (\pm 10,000)\ J\ mol^{-1} \qquad (8)$$

Ugajin *et al.* /9/ have estimated the Gibbs energy of formation of UWC_2 in the temperature range 298 to 2100 K:

$$\Delta_f G^\circ \langle UWC_2 \rangle = -184,180 - 2.9\ T\ J\ mol^{-1} \quad (9)$$

The uncertainty in their estimate is ± 10% or ± 20,000 J mol^{-1} at 1073 K. From the values of the Gibbs energies of formation of the ternary carbides estimated by Ugajin *et al.* /9/, the chemical potential of carbon over the three-phase field UC + $UWC_{1.75}$ + UWC_2 can be calculated as:

$$\Delta\mu_C = -70,628\ (\pm 35000)\ J\ mol^{-1} \quad (10)$$

These authors assumed identical entropies of formation for the two ternary carbides. Hence, the carbon potential derived from their estimates is independent of temperature. The carbon potential over the three-phase field UC + $UWC_{1.75}$ + UWC_2 determined in this study is found to be a very weak function of temperature.

The Gibbs energies of formation of the two ternary carbides derived directly from experiment are considered to be more accurate and thermodynamically consistent in the temperature range of measurement than the earlier estimates of Ugajin *et al.* /9/, which are associated with large uncertainties. Because of the relatively large uncertainty in the free energy and the narrow temperature range covered in this study, caution should be exercised in extrapolating the data significantly beyond this temperature range of measurements. Calorimetric determination of enthalpy of formation and heat capacities would be helpful in refining the data.

4. CONCLUSION

The chemical potentials of carbon in the two three-phase fields UC + $UWC_{1.75}$ + W and UC + $UWC_{1.75}$ + UWC_2 were measured in the temperature range 973 to 1173 K. By combining the measured values of the carbon potentials with auxiliary data on $\Delta_f G^\circ$ <UC> reported in the literature /10/, the Gibbs energy of formation of the two ternary carbides $UWC_{1.75}$ and UWC_2 were obtained. The data obtained in this study supersede the estimates given by Ugajin *et al.* /9/.

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