



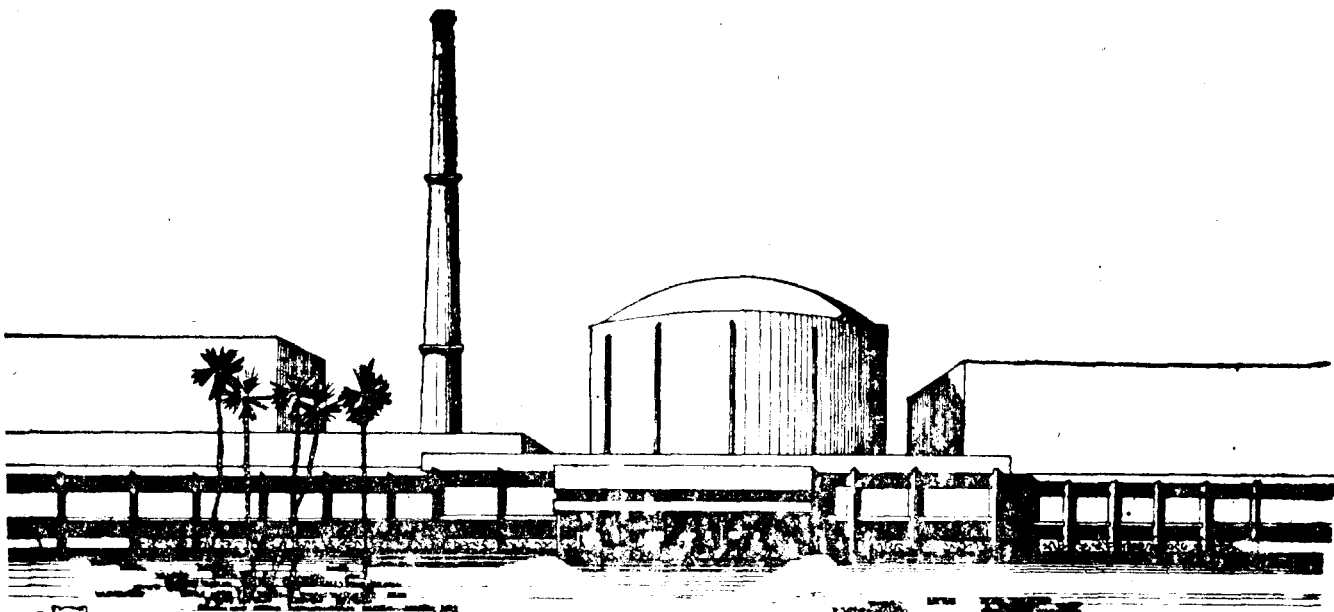
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# Carbon Potential Measurement on the Mo - MoC<sub>0.47</sub> System by Methane - Hydrogen Equilibration

*K. Ananthasivan, I. Kaliappan, V. Chandramouli, S. Anthonysamy,  
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GOVERNMENT OF INDIA,

DEPARTMENT OF ATOMIC ENERGY

**INDIRA GANDHI CENTRE FOR ATOMIC RESEARCH KALPAKKAM**

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## ABSTRACT

Uranium Plutonium mixed carbides are potential candidate fuel materials for liquid metal cooled fast breeder reactors. The carbon potential of the fuel is an important thermochemical property which strongly influences the carbon transport between the clad and the fuel. The carbon potential of the fuel is altered during irradiation of the fuel in the reactor. This is due to the formation of various fission products and their binary and ternary carbides. Molybdenum is a fission product with a high yield which can alter the carbon potential of the fuel. The present work forms part of our studies on the carbon potential measurements in the U - Mo - C ternary system. The carbon potential of the Mo-Mo<sub>2</sub>C couple measured by the methane hydrogen gas equilibration technique is presented here and the results are compared with the values cited in the literature.

KEY WORDS: [Carbon potential, fission product, carbide, heterogeneous equilibration]

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CARBON POTENTIAL MEASUREMENT ON THE Mo - MoC<sub>0.47</sub> SYSTEM BY  
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1. INTRODUCTION:

A mixed carbide of uranium and plutonium clad in AISI 316L stainless steel, is a candidate fuel for liquid metal cooled fast breeder reactors. Since carburisation of the S.S. clad by the fuel could lead to deterioration of its mechanical properties, the possibility of carbon transport from the fuel to clad deserves attention. The carbon potential of the fuel is thus one of the important factors that strongly influence the carbon transport. The carbon potential of the fuel is however likely to be altered on irradiation. As U and Pu undergo fission, a host of fission products are formed with varying tendencies for formation of binary / ternary carbides. Thus, fission products with high yield could alter the carbon balance as well as the carbon potential of the fuel, and consequently influence clad carburisation. A knowledge of the thermodynamics of U (Pu) - fission product - C systems is therefore necessary to understand or predict the evolution of the carbon potential of irradiated fuel. Various authors<sup>2-11</sup> have summarised the phase diagram data of these ternary actinide - fission product - carbon systems. However, the experimental data related to phase diagrams of these systems are limited, probably due to the difficulties encountered in synthesising and handling these alloys.

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Among the fission product elements, molybdenum is an important constituent since it has a high fission yield ( 1 at% Mo is produced at a burn up of 10 at% )<sup>2</sup>. Ugajin et.al.,<sup>12</sup> have indicated that molybdenum lowers or increases the carbon activity of uranium carbide depending on the chemical form in which it exists in the fuel. However, these conclusions were based on thermodynamic calculations. No experimental verification of the carbon activity data is available as yet over the various three phase fields in the U-Mo-C ternary system.

Our laboratory is engaged in the measurement of carbon potential as well as phase equilibria in various fuel - fission product - carbon systems. As part of these studies, measurement of the carbon activity in various phase fields of the U-Mo-C system are being carried out by using the methane-hydrogen gas equilibration technique. The present report describes the measurements on the binary system Mo-MoC<sub>0.47</sub> which forms part of the above studies.

## 2. CARBON POTENTIAL MEASUREMENTS

### 2.1. Methods for carbon activity measurement

The thermodynamic activity of carbon in a metal - metal carbide mixture of a binary system is constant at a given temperature and pressure as can be seen from the application of Gibbs phase rule. Similarly the carbon activity in a ternary metal1 - metal2 - carbon system will be fixed in those phase regions where three phases coexist at constant temperature and

pressure.

Some of the techniques used for the measurement of carbon activity are listed below:

- i) Isopiestic technique
- ii) Transpiration technique
- iii) E.m.f measurements
- iv) Heterogeneous equilibration

## 2.2 Principle of the heterogeneous equilibration technique

The heterogeneous equilibration technique involves the measurement of the thermodynamic activity of carbon in the gas phase which is in equilibrium with the solid phase. Since the solid and the gas are in equilibrium at a given temperature:

$$\text{carbon activity in gas phase} = \text{carbon activity in solid phase.} \quad \dots\dots\dots(1)$$

Now, if the free energies of formation of the gaseous components at the experimental temperature are known, then the carbon activity of the solid phase can be arrived at by just measuring the equilibrium pressures of the gaseous components. If we consider a metal carbide MC and metal M as the solid phases being equilibrated with hydrogen as an example, then we have the following equilibrium;



If the carbon solubility in the metal is negligibly small, we

\* : The following notations are used throughout the text: [ ] Solid solution component ; ( ) Gaseous species; < > Pure crystalline solid.

can represent the equilibrium constant for reaction (3) as,

$$K = \frac{p_{CH_4}}{p_{H_2}^2} \cdot a_C \quad \dots\dots\dots(4)$$

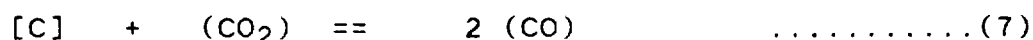
The free energy change for the this reaction at equilibrium is,

$$\Delta G = \Delta G^\circ + RT \cdot \ln K = 0 \quad \dots\dots\dots(5)$$

$$\Rightarrow RT \cdot \ln a_C = \Delta G_{fCH_4}^\circ + RT \cdot \ln K \quad \dots\dots\dots(6)$$

Thus the carbon potential ( $RT \cdot \ln a_C$ ) of the gas phase and hence the carbon activity of the condensed phase can be estimated, from such a gas - solid equilibration.

Instead of the methane-hydrogen gas mixture, CO - CO<sub>2</sub> couple can be used for equilibration. The gas solid reaction can then be represented as,



The equilibrium carbon activity can then be derived from the measured partial pressures of CO and CO<sub>2</sub> gases and the equilibrium constant for the reaction (7).

### 2.3 Advantages and disadvantages of the methane hydrogen gas equilibration technique

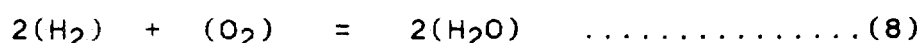
We have employed methane-hydrogen gas equilibration technique to measure the carbon activity in the Mo-C system, in this study. The main advantages of this technique are;

- i) This technique can be extended to the easily oxidisable ternary uranium-molybdenum carbides.
- ii) This technique is amenable for glove box adaptation,



which is an important prerequisite for safe handling of radioactive and chemically active samples like Pu-Mo ternary carbides.

However when methane-hydrogen equilibration technique is used to measure the thermodynamic activity of carbon it is necessary to keep the moisture level in the system very low in order to prevent the oxidation of the sample, since residual moisture increases the partial pressure of oxygen by the following reaction:



### 3 THE Mo - C SYSTEM

#### 3.1 Phase diagram data of the Mo - C system

Various authors<sup>13,15,16</sup> have reviewed the Mo-C phase diagram. Storms<sup>16</sup> and Brewer and Lamoreaux<sup>13</sup> have by and large accepted the comprehensive study of Rudy et al.,<sup>14</sup>. Brewer and Lamoreaux<sup>13</sup> have included later amendments on the phase diagram data. The various phases and the invariant points are indicated in Table I.

In the temperature range 973-1123K (where we have measured the carbon potential) for alloys of composition less than 32.5 at% C the only stable carbide of molybdenum existing in equilibrium with the metal is alpha-MoC<sub>0.47</sub><sup>13</sup>.

#### 3.2 Thermochemical data of Mo<sub>2</sub>C

Several authors<sup>18-21,25,26</sup> have measured the free energy of formation of the carbide phase which is in equilibrium with metallic molybdenum at different temperature ranges by using different techniques. Most of the measurements involve either

CH<sub>4</sub>-H<sub>2</sub> or CO/CO<sub>2</sub> heterogeneous gas equilibration. Storms<sup>16</sup>, in his compilation, recommended that the equilibrium measurements (CO-CO<sub>2</sub>) of Gleiser and Chipmann<sup>18</sup> are reliable. Hultgren et al.<sup>15</sup> rejected in their review (on the data upto 1966) all data except those of Gleiser and Chipmann<sup>18</sup>. Worrel<sup>22</sup> also arrived at a similar conclusion. Alekseev et al.,<sup>19</sup> have reported free energy values (CH<sub>4</sub>-H<sub>2</sub>) which are in agreement with those of Gleiser and Chipmann<sup>18</sup>; earlier measurements reported by Alekseev et al. were rejected by Hultgren et al.<sup>15</sup>. Browning and Emmett<sup>24</sup> reported free energy values which suggested huge entropy changes (26 eu) for the formation of Mo<sub>2</sub>C, and hence their data were rejected by the reviewers<sup>15</sup>. However, Solbakken and Emmett<sup>20</sup> (CH<sub>4</sub>-H<sub>2</sub>) reported values which were in agreement with those obtained by CO/CO<sub>2</sub> equilibration<sup>18</sup>. Brewer and Lamoreaux<sup>13</sup> in a recent compilation have accepted the values of Gleiser and Chipmann<sup>18</sup>, Solbakken and Emmett<sup>20</sup> and Alekseev<sup>19</sup>. Handa et al.<sup>21</sup> reported free energy values which were also in agreement with that of the Gleiser and Chipmann<sup>18</sup>. Brewer and Lamoreaux<sup>13</sup> have fitted the free energy data over the temperature range 298.15 - 1500 K and have given allowance for nonstoichiometry in the carbide phase. They have estimated the ΔG° for the carbide compositions MoC<sub>0.47</sub>, MoC<sub>0.4815</sub>, MoC<sub>0.487</sub> and MoC<sub>0.5</sub>. They have also listed the free energy functions, entropies and heat capacity data for all these compositions.

Brewer and Lamoreaux<sup>13</sup> have chosen, among these, MoC<sub>0.47</sub> as the carbide phase in equilibrium with molybdenum in the temperature range mentioned above, from the phase diagram information.

They have compared all the experimental data on the free energy of formation with that calculated for this composition. However, none of these authors 18-20 have mentioned the exact stoichiometry of the carbide samples used in their equilibration.

Fig 4 indicates the free energy values calculated from the heat capacity data,  $\Delta H^{\circ}_{298.15}$ ,  $\Delta S^{\circ}_{298.15}$  recommended by Brewer and Lamoreaux 13.

#### 4. EXPERIMENTAL

##### 4.1. Inert atmosphere glove box system

The carbides of uranium are pyrophoric and are susceptible to oxidation and hydrolysis. Therefore, the entire carbon potential measurement has to be carried out in an inert atmosphere (argon) glove box system with a minimum amounts of oxygen and moisture in the ambience.

An inert atmosphere glove box system was used for this purpose, a schematic diagram of which is given in Fig. 1. The argon gas in the box was continuously recirculated at a rate of 2 to 3 m<sup>2</sup> / hr. through a purification tower to maintain the oxygen and moisture concentration in the box atmosphere at low levels. The purification tower contains molecular sieves and a copper based deoxo catalyst which remove the moisture and oxygen respectively. To limit the inleakage of air and moisture into the glove box through the gloves and other leak points, the glove box was maintained at a positive pressure with respect to the external atmosphere. The argon gas, even after such a purification, still contained oxygen and moisture impurities of the

order of 20 to 30 ppm. To bring down the impurity concentration to about 10 ppm or below, a molten sodium bath was kept inside the box. The bath serves as a getter of oxygen, as well as an indicator of the purity of the inert atmosphere.

#### **4.2. Experimental assembly**

A schematic diagram of the experimental assembly used for carbon potential measurement is shown in Fig. 1. It consists of a high purity, recrystallised, one-end-closed alumina tube of 300 mm length and 25 mm dia to which a gas inlet and an outlet are connected. There is also a provision for sampling the gas inside the tube. The sample is placed inside this tube in a quartz sample holder and is heated under hydrogen atmosphere. The hydrogen gas (IOLAR2 grade supplied by M/s. I O L Madras) containing 4ppm each of moisture and oxygen is further purified by passing it through a cold trap consisting of a molecular sieve at liquid nitrogen temperature.

#### **4.3. Sample preparation**

In the present study we prepared a two phase mixture of Mo and  $\text{MoC}_{0.47}$  by arc melting bits of 99.9% pure moly wire with spectroscopic grade graphite and annealing the product at 1073 K for 48 hrs in flowing argon. The sample was then characterized by X ray diffraction ( for phase identification ) and oxygen and carbon analysis. The oxygen content was determined by using the inert gas fusion technique while the carbon content was estimated by combustion of the sample in flowing oxygen followed by estimation of the evolved  $\text{CO}_2$ . Typical values of oxygen and carbon content are; oxygen: less than 2000 ppm and carbon: 3.484 wt%.

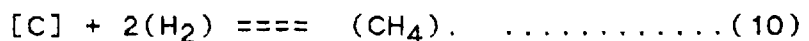
The XRD pattern of a typical sample is shown in Fig. 2. which indicates only the presence of Mo and MoC<sub>0.47</sub> as suggested by the Mo - C phase diagram (Fig. 3). No oxide phases were found.

#### 4.4. Experimental Procedure:

The equilibration was performed in a closed system where the gas mixture is subjected to a thermal gradient. Hence, there could be segregation of the gases due to thermal diffusion. However, we experimentally confirmed the absence of any significant thermal segregation in our system. To do this, a methane-hydrogen mixture of known composition was maintained at the experimental temperature in the system, for about 48hrs and samples ( 100 micro litres ) were withdrawn periodically from the reactor and analysed for methane. It was found that the methane concentration did not vary with time, which suggested that thermal diffusion effects were not significant in our system. Identical results were obtained when the experiment was performed with and without recirculation of the gas mixture.

During the equilibration experiment, high purity hydrogen was allowed to react with the sample at the desired temperature in the alumina reactor in which the gas mixture was constantly recirculated.

The equilibrium reaction can be represented as



To detect the methane produced in this reaction, gas chromatographic analysis was used. For the quantitative estimation of the methane gas in the gas samples withdrawn from the alumina tube reactor at regular intervals, a Flame Ionization

Detector was used. The amplified millivolt signal from the electrometer was recorded and integrated by using a digital peak area integrator (CR 3A supplied by M/s. Shimadzu Corporation of Japan). Attainment of equilibrium was assumed when the methane concentration remained invariant for more than 20 hrs. Subsequently, the equilibrium was disturbed by flushing hydrogen through the alumina reactor. Once again methane concentration was allowed to build up and reach constancy. In all the measurements the latter value agreed with the former. Thus the attainment of equilibrium was reaffirmed.

## 5. RESULTS AND DISCUSSION

Our carbon potential values ( 973 - 1123 K ) for molybdenum - molybdenum carbide ( $\text{MoC}_{0.47}$ ) mixture are given in Table II. The carbon potential of the Mo-Mo<sub>2</sub>C couple as a function of temperature measured by various authors is presented in Fig 4. Our data has an uncertainty of about  $\pm 2$  kJ, which stems from the uncertainty in the measurement of methane concentration. It is seen that the slope of the free energy vs. temperature plots of our values are in agreement with that of Gleiser and Chipmann's<sup>18</sup> and with that of the evaluated free energy fit of Brewer and Lamoreaux<sup>13</sup>.

Free energy of formation equations for  $\text{MoC}_{0.47}$  quoted by various authors in the respective temperature ranges, is given in Table III. Table IV gives the free energy values for  $\text{MoC}_{0.47}$  calculated from Brewer and Lamoreaux<sup>13</sup> compilation, in the temperature range of 973 to 1273 K.

The third law enthalpies calculated from our  $RT \ln K$  values are given in Table V. The free energy functions for molybdenum and molybdenum carbide were taken from Brewer and Lamoreaux's compilation<sup>13</sup>, while those for methane and hydrogen were obtained from JANAF tables<sup>24</sup>. The third law enthalpy  $\Delta H^\circ$  of  $\text{MoC}_{0.47}$  obtained from our experimental data ( at different temperatures ) was constant within the limits of experimental error. This indicates that our measurements are free from temperature dependent systematic errors.

The third law enthalpies obtained by various authors are indicated in Table VI.

## 6. CONCLUSION

The value for the free energy of formation of  $\text{Mo}_2\text{C}$  cited in the literature is based on the measurements which were carried out by using samples of  $\text{Mo}_2\text{C}$  for which the exact stoichiometry was not reported. In the present study we have measured the carbon potential of the molybdenum carbide phase in equilibrium with metallic molybdenum in the temperature range 973 - 1173 K. The slope of the  $G_f^\circ$  vs. T plot from our measurements agreed well with the values cited in the literature. The third law enthalpies indicated that the measurement is free from temperature dependent systematic errors. However, the free energy of formation of  $\text{Mo}_2\text{C}$  evaluated from our measurement is about 8 kJ / mol more positive than the value cited in the literature.

## 7. REFERENCES

1. Ganguly, C., BARC, Bombay, India. Studies on the preparation and sintering of uranium plutonium monocarbide, mononitride and monocarbonitride. Ph.D., thesis, University of Calcutta (1979).
2. Benedict, U., Euratom Report EUR-5766e(1977)Part I & EUR-5766e Part II (1977).
3. Holleck, Helmut., Handbook on the physics and chemistry of actinides, edited by A.J. Freeman and C. Keller, Elsevier Science Publishers B.V. 1986. p 209.
4. Benedict, U., Thermodynamics of nuclear materials 1979, Vol I, (IAEA, Vienna 1980 )p 543.
5. Holleck, H., & Kleykemp, H., Journal of Nuclear Materials 32(1969)1.
6. Holleck, H., Thermodynamics of Nuclear Materials 1974, Vol I (IAEA, Vienna, 1975)p. 45.
7. Smalios, E., German Report KfK-1953(1974).
8. Holleck, H., German Report KfK-3087B (1981); Journal of Nuclear Materials 124 (1984) 129.
9. Haines, H.R., & Potter, P.E., in: Thermodynamics of Nuclear Materials 1974, Vol I (IAEA, Vienna, 1975)p. 45.
10. Lorenzelli, N French Report CEA-R 4455 (1973).
11. Fee, C.C., & Johnson, C.E., US Report ANL-AFP-10 (1975).
12. Ugajin, M., Journal of Nuclear Science and Technology 12(6) pp 381-384.
13. Brewer & Lamoreaux. Molybdenum: Physicochemical properties of its alloys and compounds, Ed. L. Brewer, Atomic Energy Review, Special Issue No. 7, (IAEA), Vienna.
14. Rudy, E., et al., Transaction of the metallurgical society of AIME Vol. 239 (1967) 1247.
15. Hultgren, R., et al., Selected Values of the Thermodynamic Properties of Binary Alloys, American Society for Metals, Metals Park, Ohio(1973)7/66
16. Storms, E.K., The Refractory Carbides, Refractory materials, A series of Monographs Vol-2. Academic Press (1967).



17. Binary Alloy Phase Diagrams, Vol. 1., 1986.  
Ed. Masalski, Thaddeus B., American Society for Metals, Metals  
Park, Ohio, U.S.A.
18. Gleiser, M., & Chipman, J.J., Phys. Chem. 66(1962) 1539-40
19. Alekseev, V.I., Surovoi, Yu.N., Shvartsman, L.A., Poroshk.  
Metall. 7 9 (1967) 64-70.
20. Solbakken, A. & Emmet, P.H., Journal of American Chemical  
Society 91 (1969) 31-34.
21. Handa, M., et al., J. of Nuclear Materials 116 (1983) 178-183.
22. Worrel, W.L., Trans. Metall. Soc. AIME 233(1965) 1173-77.
23. JANAF Thermochemical Tables, 3<sup>rd</sup> ed., Eds., M.W. Chase, C.A.  
Davies, J.R. Dourey, D.J. Frury, R.A. McDonald and A.N. Syverud,  
J. Phys. Chem., Ref. data 14 (1985).
24. Browning, L.C. and Emmett, P.H. J. Am. Chem. Soc., 74, 4773  
(1952)

Table I  
Phases and Eutectics of the Mo-C system

Phase	Maximum comp. range (at% C)	Melting or decomposition temperature (K) Composition (at% C)
Mo (cI2)	0-1.1	m2890 ± 8
α Mo2C (hP3)	26-36	m2795 ± 5, 34 ± 0.3%
β Mo2C (oP12)	31.7-32.7	tr703 ± 30, 32.5 ± 0.1%
Mo3C2 (hP 10)	37.0-39.5	d1928±15, 39 ± 0.5%
		m2823 ± 5, 38.6 ± 0.3%
α MoC 1-x (cF8)	39.5-43	d2233 ± 5, 40.4 ± 0.4%
		m2873 ± 5, 42.0 ± 0.3%
γ MoC (hP2)	50	p1423 ± 40, 50%

Eutectics

Solid Phases	Temperature	Liquid composition (at% C)
Mo - α Mo2C	2478 ± 5	17 ± 2
α Mo2C - Mo3C2	2783 ± 5	36.3 ± 0.3
Mo3C2 - α MoC1-x	2820 ± 5	39.5 ± 0.3
α MoC1-x	2857 ± 5	45 ± 1

TABLE II

CH<sub>4</sub>/H<sub>2</sub> Equilibrium measurements on Mo/MoC<sub>0.47</sub> alloys.

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TEMP (K)	CARBON POTENTIAL kJ / mol
973	-45.9051
973	-45.2424
1023	-47.9348
1023	-48.2583
1073	-49.0992
1073	-50.1190
1073	-49.6628
1073	-45.8428
1073	-45.9069
1073	-46.2734
1073	-44.7186
1123	-47.5675

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XRD: Mo & Mo<sub>2</sub>C Phases present: Free C & Oxides of Mo not detected.O<sub>2</sub> Analysis: less than 2000 ppm.

TABLE III

Free energy of formation equations for  $\text{MoCo}_{.47}$ 

AUTHOR	TEMPERATURE RANGE	FREE ENERGY EQUATION $\Delta G_f^\circ = A + B * T$
Gleiser and Chipmann <sup>18</sup>	1200 - 1340 K	-48995 - 7.66 * T
Solbakken and Emmet <sup>20</sup>	873 - 1173 K	-50334 - 6.03 * T
Brewer and Lamoreaux <sup>13</sup>	298 - 1500 K	-46434 - 9.71 * T
This work	973 - 1173 K	-37764 - 8.41 * T

TABLE IV

Standard Free energy of formation of  $\text{MoC}_{0.47}^{13}$

TEMP (K)	$\frac{H^{\circ}}{T}$ J/mol	$\frac{S^{\circ}}{T}$ J/K/mol	$\frac{G^{\circ}}{T}$ J/mol	$2.12766 * \frac{G^{\circ}}{T}$ J/g.atom C
973	-21245	5.3149	-26416	-56433
1023	-21131	5.4296	-26685	-56776
1073	-21019	5.5363	-26960	-57359
1123	-20910	5.6350	-27238	-57954
1173	-20805	5.7271	-27522	-58558
1223	-20702	5.8124	-27811	-59172

TABLE V

Third Law enthalpies for  $\text{MoC}_{0.47}$  from our measurements

TEMP	T * $\Delta f_{ef}$	$\Delta G^\circ$	$\Delta H^\circ_{298.15}$	.47 * [ $\Delta H^\circ_{298.15}$ ]
	kJ/mol	kJ/mol	J/mol	J/g.atom C
973	-92.622	-61.415	-31.206	-17.622
973	-92.622	-61.506	-31.116	-17.665
1023	-97.977	-69.759	-21.218	-18.664
1023	-97.977	-70.082	-27.895	-18.816
1073	-97.977	-76.484	-26.803	-18.316
1073	-111.059	-77.504	-25.783	-19.419
1073	-111.059	-77.047	-26.240	-19.205
1073	-111.059	-73.291	-29.996	-17.440
1073	-111.059	-73.658	-29.629	-17.612
1073	-111.059	-72.103	-31.184	-16.874
1123	-117.215	-80.517	-28.026	-17.942
Mean ( This work )		-18.143 kJ/g atom C		
Gleiser & Chipmann <sup>18</sup>		-21.903 kJ/g atom C		
Alekseev et.al. <sup>19</sup>		-21.861 kJ/g atom C		
Solbakken & Emmett <sup>20</sup>		-23.410 kJ/g atom C		

TABLE VI

Enthalpy of Formation of  $\text{MoC}_{0.47}$  derived at by third law analysis of our experimental data.

Author	Enthalpy at 298.15 K obtained by third law analysis (in joules)
Gleiser and Chipmann <sup>18</sup>	-21903
Alekseev <sup>19</sup>	-21861
Solbakken and Emmet <sup>20</sup>	-23410
This work	-18142

The free energy functions for  $\text{MoC}_{0.47}$  and Mo were obtained from reference 13 while the free energy functions for  $\text{CH}_4$  and  $\text{H}_2$  were obtained from JANAF Tables<sup>23</sup>.

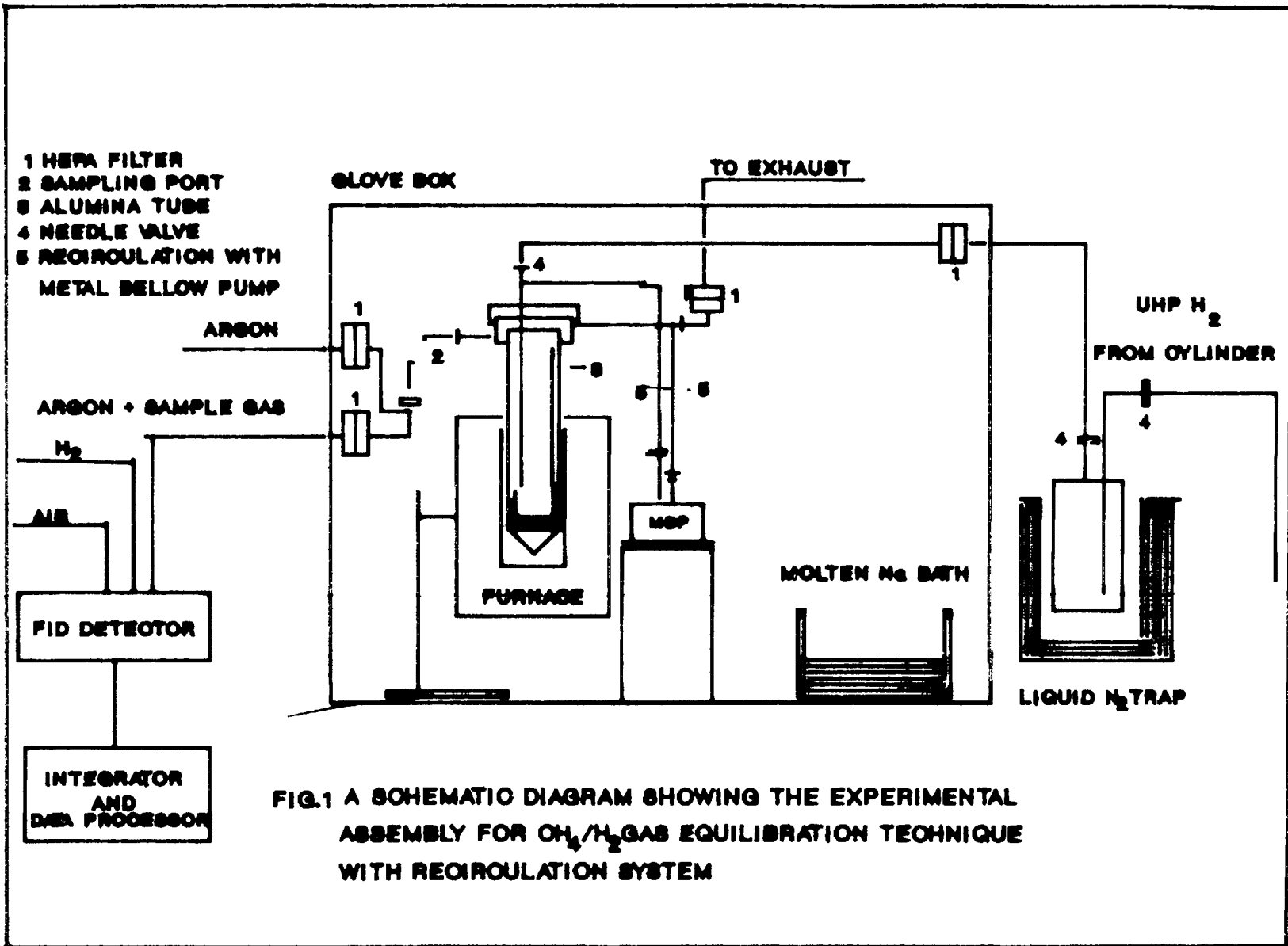
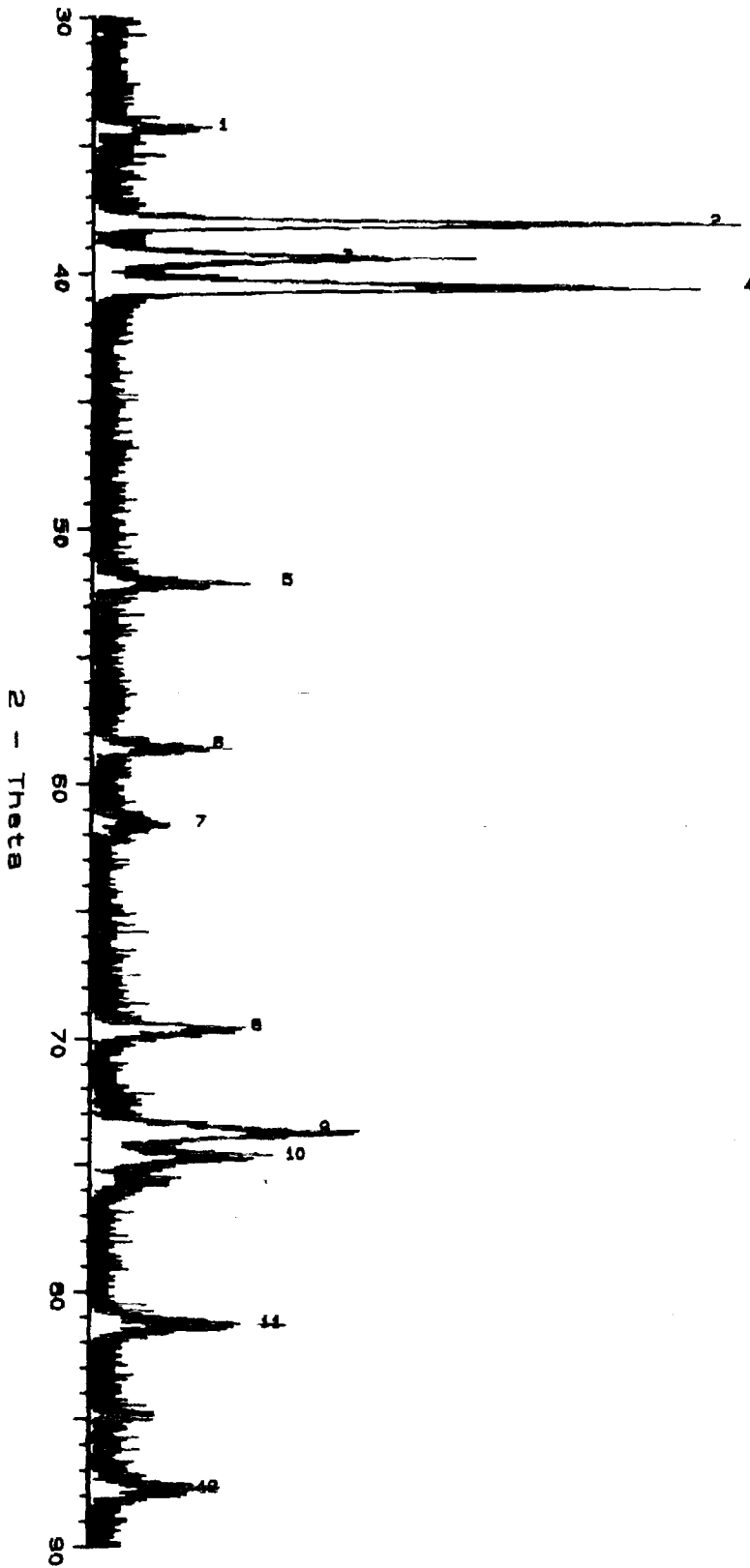




Fig. 2 XRD pattern of Mo - MoZrC two phase alloy



No.	2-Theta	d-Value	Rel.I
1	34.380	2.6098	13.8
2	36.080	2.3531	66.1
3	38.450	2.2841	32.7
4	40.610	2.2218	81.1
5	52.160	1.7528	23.8
6	58.580	1.5782	11.9
7	61.640	1.5047	10.8
8	68.620	1.3504	17.8
9	73.680	1.2857	29.7
10	74.720	1.2704	22.6
11	81.310	1.1633	20.8
12	87.780	1.1122	9.9

**FIG\_3 Mo-C PHASE DIAGRAM**

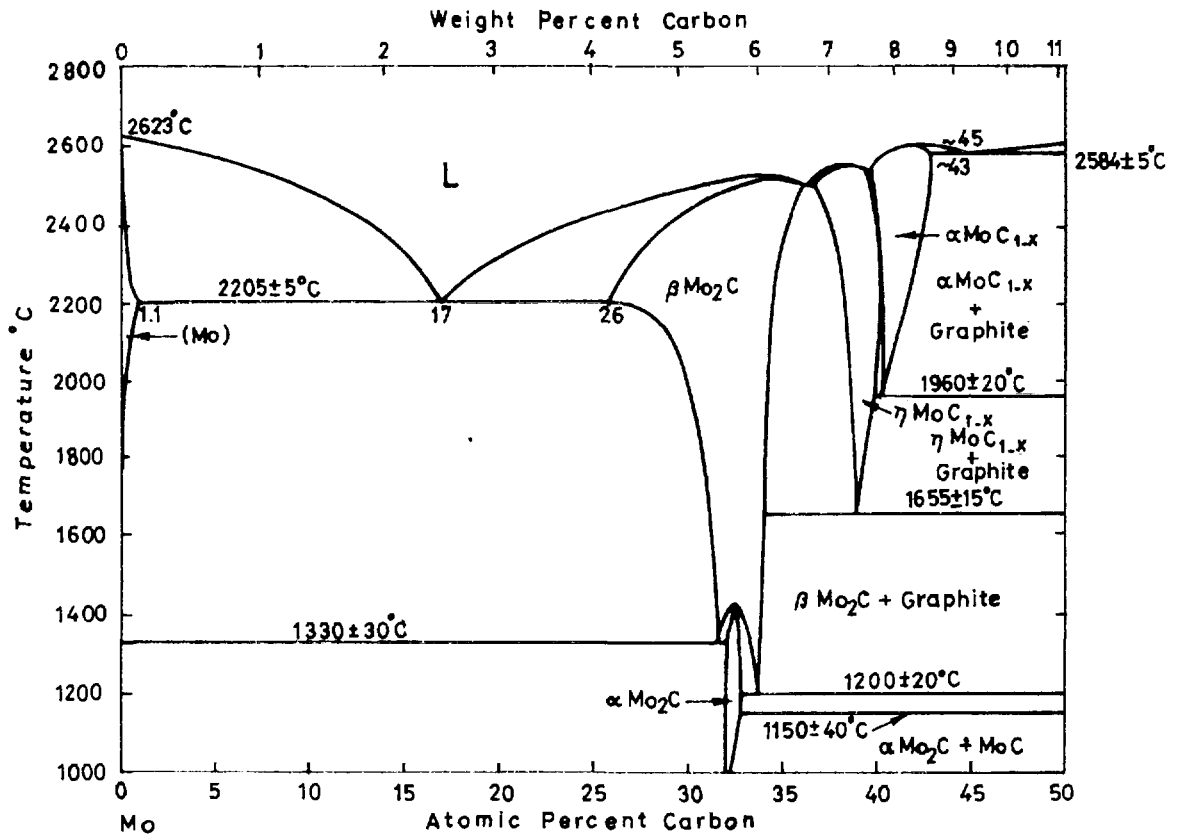


Fig.4 CARBON POTENTIAL OF Mo-MoC<sub>0.5</sub> SYSTEM

