

Preparation of tungsten carbide by decomposition of $W(CO)_6$. I. Thermodynamic calculations in the system $W-C-O$

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The paper deals with the thermodynamic calculations in the ternary system $W-C-O$ at 600, 800, and 1000 K, with the aim to find the stability regions of the phases which can be present. The calculation of stability regions of the phases diagrammatically represented in the plots with $\log p_{CO} - \log p_{CO_2}$ coordinates made it possible to choose the experimental conditions of the decomposition of tungsten carbonyl so that the required final product is obtained. From the thermodynamic point of view the conditions of preparation of non-stoichiometric tungsten carbide with catalytic activity for oxidation of hydrogen are discussed in detail.

Настоящая работа описывает термодинамические расчеты в трехкомпонентной системе $W-C-O$ при температурах 600, 800 и 1000 К с целью найти области стабильности фаз, которые могут присутствовать. Значение вычисленных областей стабильности фазей графически представленных зависимостями $\log p_{CO} - \log p_{CO_2}$ состоит в возможности выбора экспериментальных условий разложения карбонила вольфрама таким образом, чтобы получить требуемый конечный продукт. Условия приготовления нестехиометрического карбида вольфрама с каталитической активностью для окисления водорода обсуждаются детально с термодинамической точки зрения.

The application of metal carbonyls for preparation of pure powder materials and thin films has attained a great significance mainly due to the fact that the sum of impurities present in carbonyl materials attains a maximum of 10^{-3} per cent which means that all final products prepared from them are of a higher purity than those prepared by various other methods [1, 2].

The preparation of tungsten carbide has been frequently discussed in the literature since it is one of the basic compounds of the modern tool materials, and also due to the fact that non-stoichiometric tungsten carbide has a catalytic activity for oxidation of hydrogen in acid electrolyte.

From the phase diagram of the binary system $W-C$ [3] it is evident that the system contains three intermediate phases:

- subcarbide, W_2C , with a congruent melting point and a hexagonal lattice;
- carbide, WC , with a hexagonal lattice formed by decomposition of W_2C ;
- carbide, $\alpha-WC_{1-x}$, with a cubic lattice, stable only at temperatures above $2530^\circ C$ and a carbon deficiency.

For the preparation of non-stoichiometric metastable tungsten carbide with cubic lattice various methods and various starting materials have been used. For this preparation *Svatá* and *Zábranský* [4] have used powder tungsten, tungsten trioxide and white modification of tungstic acid and the carburization was realized in an atmosphere of carbon monoxide. *Babad et al.* [5] prepared non-stoichiometric tungsten carbide with cubic planicentric lattice by a decomposition of tungsten hexacarbonyl in a hydrogen atmosphere at 400°C. The preservation of the symmetry and lattice parameters at a decreasing carbon content in this phase can be elucidated by various lattice defects, mainly vacancies, in the carbon sublattice [5, 6]. The mechanism of the formation of this metastable non-stoichiometric tungsten carbide by decomposition of $W(CO)_6$ has not yet been explained. *Krivoruchko* and *Salagovich* [7] have discovered that the carbon content of carbide prepared in this way decreases considerably with increased temperature of the core on which tungsten carbide is formed. *Toryanik et al.* [8] assumed that the metastable carbide phase is formed as a result of an incomplete decomposition of $W(CO)_6$ with the preservation of carbon in bound form. They have also disclosed that with an increase of temperature of decomposition the lattice parameter of carbide decreases which is accompanied by a lowering of its carbon content.

In order to elucidate the possibilities of the preparation of tungsten carbide with a non-stoichiometric composition by the decomposition of $W(CO)_6$ from the point of view of thermodynamics and to calculate the stability regions of various phases which may be formed during this decomposition, a thermodynamic evaluation of the ternary system W—C—O was carried out.

Thermodynamic evaluation

The decomposition of tungsten carbonyl can be described by the ternary system W—C—O due to the fact that the equilibrium of the reaction



is shifted strongly to the right, its equilibrium constant at 400 K being 1.43×10^9 [8]. Since the thermodynamic values for reaction (1) above 400 K are not available, it was supposed that tungsten carbonyl was completely decomposed at higher temperatures. Due to the lack of thermodynamic data for non-stoichiometric tungsten carbide with a cubic lattice, it is assumed that from the thermodynamic point of view it has the same properties as hexagonal tungsten carbide. In thermodynamic calculations the

Table 1

Values of equilibrium constants for reactions of phase formation considered in Figs. 1—3

No.	Reaction	$\log K_{600}$	$\log K_{800}$	$\log K_{1000}$
2	$W + 2CO_2 = WO_2 + 2CO$	+1.467	+1.035	+0.855
3	$WO_2 + CO_2 = WO_3 + CO$	-2.138	-1.342	-0.912
4	$W + 2CO = WC + CO_2$	+8.977	+4.368	+1.622
5	$WO_2 + 4CO = WC + 3CO_2$	+7.510	+3.303	+0.767
6	$WO_3 + 5CO = WC + 4CO_2$	+9.548	+4.645	+1.679

reactions of tungsten oxides in vapour phase were neglected since their partial pressures in the considered temperature range are very low.

Taking into account the above assumptions, the reactions summarized in Table 1 were considered for thermodynamic calculations. Here also the logarithms of their respective equilibrium constants are given. Thermodynamic data were taken from the literature [9]. These reactions and their equilibrium constants were used for the calculation of the stability regions of the phases in a CO—CO₂ atmosphere at temperatures 600, 800, and 1000 K. The stability regions are plotted in Figs. 1—3 in the log p_{CO} —log p_{CO_2} coordinates as areas bordered by the lines which represent the respective reaction (Table 1).

Let us discuss in detail the existence of individual phases in the ternary system W—C—O with regard to the degrees of freedom. According to the Gibbs' phase rule

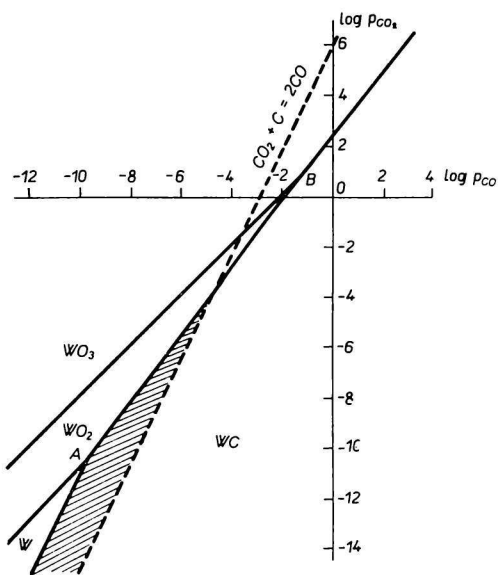


Fig. 1. The system W—C—O at 600 K.

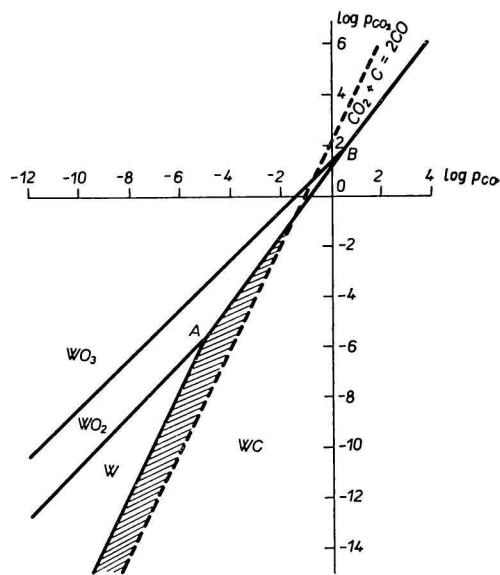


Fig. 2. The system W—C—O at 800 K.

$$f = k - p + 2,$$

where f = number of degrees of freedom,

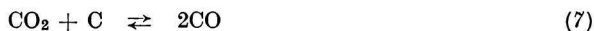
k = number of components,

p = number of phases,

for reactions 2 and 3 (Table 1) where two solid phases coexist with a gaseous phase the ternary system is bivariant which means that two parameters, in this case temperature and one partial pressure, can be changed independently (the second partial pressure is given by the coordinate of the point on the line representing the reaction). The same consideration holds also for the reactions of the formation of tungsten carbide (reactions

3 to 5, Table 1) where the system is bivariant. For points *A* and *B*, Figs. 1–3, three solid phases coexist with a gaseous phase and the system is monovariant which means that only temperature can be chosen whereas the composition of the atmosphere above the solid phase is given by the coordinates of points *A* and *B*, respectively.

In gaseous phase composed of CO and CO₂ the following reaction takes place in the presence of solid carbon



the equilibrium constant of which is given by the relation

$$K_7 = \frac{p_{\text{CO}}^2}{p_{\text{CO}_2}}$$

The values of the equilibrium constant K_7 at temperatures 600, 800, and 1000 K are 1.74×10^{-6} , 10^{-2} , and 1.76, respectively [9]. Reaction (7) for the system C–O is in diagrams (Figs. 1–3) represented by a dashed line which divides the area into two halves. On the left-hand side, the reaction (7) proceeds with the formation of carbon monoxide while on the right-hand side the reaction proceeds in the opposite direction producing carbon dioxide and carbon.

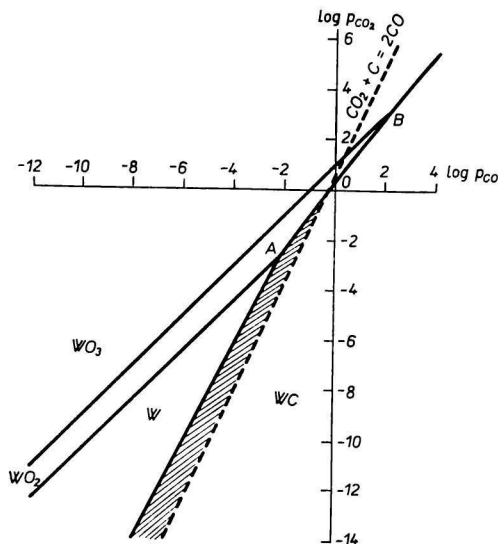


Fig. 3. The system W–C–O at 1000 K.

Discussion

The significance of the calculated diagrams with $\log p_{\text{CO}}-\log p_{\text{CO}_2}$ coordinates based on the thermodynamic data lies in the fact that they make it possible to determine the stability regions of phases which can be formed in the ternary system W–C–O.

From Figs. 1—3 it follows that with an increasing temperature the spread of the stability region of metallic tungsten increases. Simultaneously, point *A* representing the three-phase equilibrium in the W—C—O system is shifted towards higher p_{CO} and p_{CO_2} . Apart to this we can see that the WO_2 stability region becomes narrower whereas the extension of the WO_3 stability region with increasing carbon monoxide partial pressures is not very significant.

The calculated diagrams allow to choose the experimental conditions (temperature, composition of the gaseous phase) in such a way that tungsten carbide can be prepared as final product of the decomposition of $W(CO)_6$. The kinetic factors of the reactions involved and the additional factors such as surface energy in connection with the particle size, lattice defects, *etc.* have not been considered in the calculation. According to authors' opinion the carbon content in tungsten carbide, *i.e.* its deviation from the stoichiometric composition might be governed by the reaction



therefore the region in which the experimental conditions of the preparation of non-stoichiometric tungsten carbide should be chosen, is reduced to the shaded area (Figs. 1—3). From a comparison of the diagrams it follows that with an increased temperature this region becomes narrower which means that the most suitable would be the temperatures between 600 and 800 K.

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