

# Formation of NbC and TaC by solid-state reaction

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The formation of NbC and TaC by solid-state reaction of Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> with carbon, respectively, was studied at 1000 to 1285° C by X-ray diffraction. Factors affecting the formation of the carbides, such as the nature of the reaction vessel, the molar ratio of carbon/oxide, the form of reactant carbon, etc., were examined. By covering the graphite crucible and increasing the molar ratio of carbon to oxide, complete formation of NbC and TaC could be achieved in about 60 min at low temperatures (1170 and 1225° C, respectively). The beneficial effect of covering the crucible is ascribed to the retention of CO which facilitates the reaction at low temperatures. The formation kinetics of NbC and TaC obey a first-order equation, with activation energies of 90 and 93 kcal mol<sup>-1</sup>, respectively. Possible mechanisms for the solid-state reactions are discussed.

## 1. Introduction

Niobium and tantalum carbides, NbC and TaC, are materials with very high melting points (>3500° C) and a high resistance to chemical attack or thermal shock, which makes them useful for high temperature and high stress engineering applications. These carbide powders have previously been produced by direct reaction of niobium and tantalum metal with carbon, gas phase reaction of NbCl<sub>5</sub> and TaCl<sub>5</sub> with hydrocarbon [1, 2], or solid-state reaction of Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> with carbon [3, 4]. It has been reported that formation of the carbides by the solid-state reaction proceeds at high temperature (>1400° C) under high vacuum, but higher temperatures (>1500° C) are necessary for complete reaction [5]. However, factors facilitating the reaction, such as the reaction vessel, the molar ratio of carbon/oxide, the form of carbon, etc. have not been discussed previously, neither has the reaction mechanism previously been considered. In this paper, the most favourable conditions are determined, under which it has been possible to produce NbC and TaC at relatively low temperatures, and the reaction mechanism under these conditions is deduced from kinetic considerations.

## 2. Experimental procedure

The starting oxides were niobium and tantalum pentoxide (Mitsuwa Kagaku Co., 99.9% purity) with an average particle size of 0.2 and 0.5 μm, respectively. Active carbon and graphite (both are obtained from Kanto Kagaku Co.) were used as a source of carbon. The former was composed of fragile plate-like agglomerates (10 to 30 μm) with very fine particles (0.05 μm) while the latter was composed of imbricate particles (10 to 50 μm). Mixtures of the oxide and carbon powders with molar ratios of carbon/oxide = 7 to 12 were well mixed in an agate mortar. The mixture was placed in an alumina or graphite boat (10 cm × 2 cm × 1 cm), or graphite crucible (20 cm × 12<sup>φ</sup> mm), introduced into a tube furnace maintained at fixed temperatures of 1170 to 1285° C in a flowing atmosphere of argon or mixture of argon and hydrogen (100 ml min<sup>-1</sup>), and held at these temperatures for 120 min. The formation of NbC and TaC in the samples obtained under the above conditions were studied by XRD (X-ray diffraction), and the relative peak height, *R*, of NbC or TaC was used as a measure of the fractional conversion of the carbides according to Equation 1

TABLE I Experimental results for the formation of NbC by reaction of Nb<sub>2</sub>O<sub>5</sub> with carbon

Run number	Reaction vessel	Ratio of C/Nb <sub>2</sub> O <sub>5</sub>	Atmosphere	R(%)
1	Al <sub>2</sub> O <sub>3</sub> boat	7	Argon	40
2	Al <sub>2</sub> O <sub>3</sub> boat	7	Ar + H <sub>2</sub> *	60
3	Al <sub>2</sub> O <sub>3</sub> boat	7	H <sub>2</sub>	40
4	Graphite boat	7	Ar + H <sub>2</sub> *	52
5	Graphite crucible	7	Ar + H <sub>2</sub> *	80
6	Graphite crucible	10	Ar + H <sub>2</sub> *	90
7	Graphite crucible	12	Ar + H <sub>2</sub> *	95
8	Covered graphite crucible	7	Argon	95
9	Covered graphite crucible	10	Argon	100

\*Volume ratio: 1:1, source of carbon: active carbon, temperature: 1285°C, time: 120 min.

$$R(\%) = I_{\text{carbide}} / (I_{\text{carbide}} + I_{\text{oxide}}) \quad (1)$$

where  $I_{\text{carbide}}$  = the (111) peak height of carbide and  $I_{\text{oxide}}$  = the (001) peak height of Nb<sub>2</sub>O<sub>5</sub> or Ta<sub>2</sub>O<sub>5</sub>.

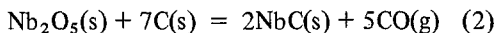
In order to obtain kinetic data for the formation of NbC and TaC, experiments on the reaction of Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> with a 10-fold content of active carbon were also carried out at 1100 to 1200°C for 0 to 120 min in argon using a covered graphite crucible. The onset of the reaction was taken as the time when the sample was introduced into a furnace held at a fixed temperature. The fractional conversion ( $\alpha$ ) of NbC was determined by quantitative X-ray analysis in which the (111) peak area of NbC was compared with the (200) peak area of MgO added as an internal standard. In the case of TaC, the  $\alpha$  values were semiquantitatively determined from the relative peak heights,  $R$ , according to Equation 1.

### 3. Results and discussion

#### 3.1. Formation of NbC

##### 3.1.1. Factors affecting the formation of NbC

Table I shows the influence of reaction vessel, ratio of C/Nb<sub>2</sub>O<sub>5</sub> and atmosphere on the formation of NbC by reaction of Nb<sub>2</sub>O<sub>5</sub> with active carbon. When the molar ratio of C/Nb<sub>2</sub>O<sub>5</sub> = 7, the reaction could proceed according to Equation 2, since CO is expected to form at temperatures over about 700°C, according to the thermodynamic data [6].



where s is solid and g is gas. The experiments in a hydrogen-containing atmosphere using an

Al<sub>2</sub>O<sub>3</sub> boat give a higher value of  $R$  than in pure argon, probably due to hydrogen reduction of niobium oxide, but pure H<sub>2</sub> gives no improvement over pure argon (Runs 1 to 3). The graphite boat gives similar results to the Al<sub>2</sub>O<sub>3</sub> boat, but the use of a graphite crucible exceedingly increases NbC formation (Run 4 and 5). Furthermore, covering the crucible causes the formation of NbC to increase to  $R = 95\%$  without the need for a hydrogen-containing atmosphere (Run 8). Increasing the molar ratio of C/Nb<sub>2</sub>O<sub>5</sub> also increases the degree of NbC formation (Runs 5 to 7 and 8, and 9). The formation of NbC was found to be complete after 120 min at 1285°C when the crucible was covered and the molar ratio was 10 (Run 9). The influence of the form of carbon and reaction temperature on the formation of NbC are shown in Fig. 1, which was obtained

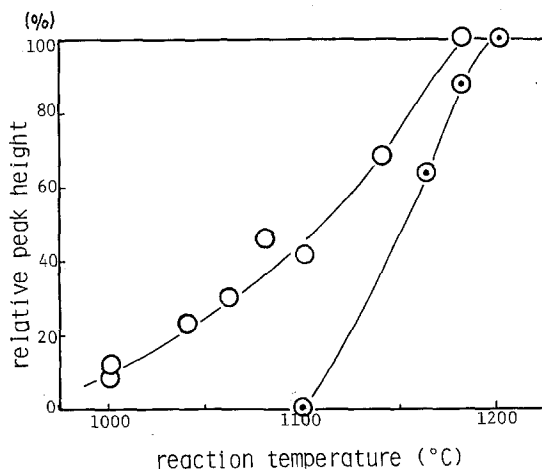


Figure 1 Influence of the form of carbon on the formation of NbC. ○: active carbon, ◐: graphite, reaction time: 50 min.

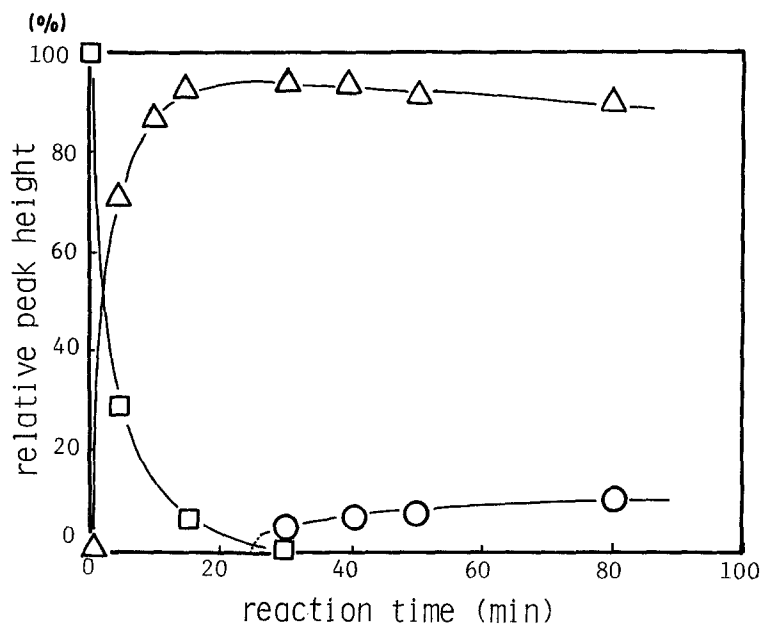
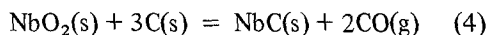
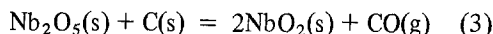


Figure 2 Changes of relative X-ray peak height of Nb<sub>2</sub>O<sub>5</sub>, NbO<sub>2</sub> and NbC with reaction time at 1000° C. ○: NbC, △: NbO<sub>2</sub>, □: Nb<sub>2</sub>O<sub>5</sub>.

under the same conditions as those of Run 9. Compared with graphite, active carbon facilitates the formation of NbC particularly in the initial stages below 1000° C. The formation is seen to be complete at 1180 and 1200° C in the case of active carbon and graphite, respectively.

Fig. 2 shows changes of the relative X-ray peak heights of Nb<sub>2</sub>O<sub>5</sub>, NbO<sub>2</sub> and NbC with time, for the reaction at 1000° C in argon under the same conditions as in Run 9. No low-niobium oxide other than NbO<sub>2</sub> nor niobium was detected by XRD. Nb<sub>2</sub>O<sub>5</sub> rapidly decreases with the rapid formation of NbO<sub>2</sub> in the initial 30 min period.

The NbO<sub>2</sub> then gradually decreases with the gradual increase of NbC, which appears after about 30 min reaction time. These facts indicate that Nb<sub>2</sub>O<sub>5</sub> is almost reduced to NbO<sub>2</sub> in the initial period, followed by the formation of NbC. Thus, the formation of NbC by reaction of Nb<sub>2</sub>O<sub>5</sub> with carbon must occur according to Equations 3 and 4,



Since reactions 3 and 4 proceed with the evolution of CO gas, covering the crucible is assumed to

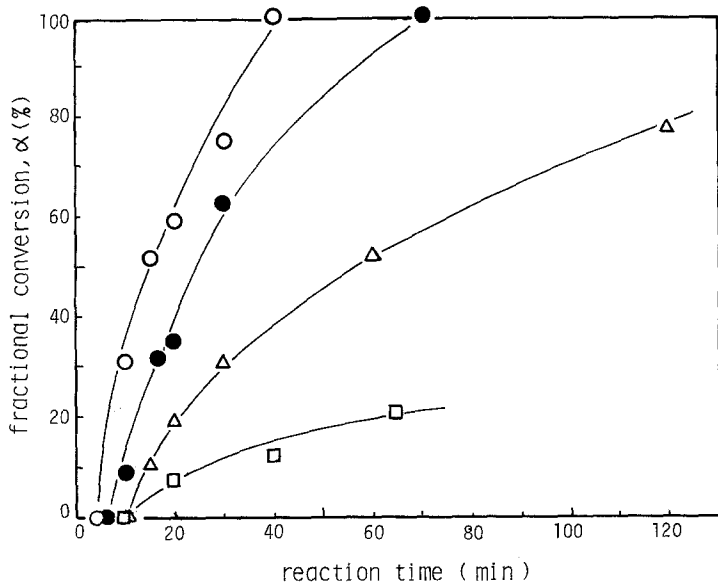


Figure 3 Formation rates of NbC. ○: 1200° C, ●: 1170° C, △: 1130° C, □: 1100° C.

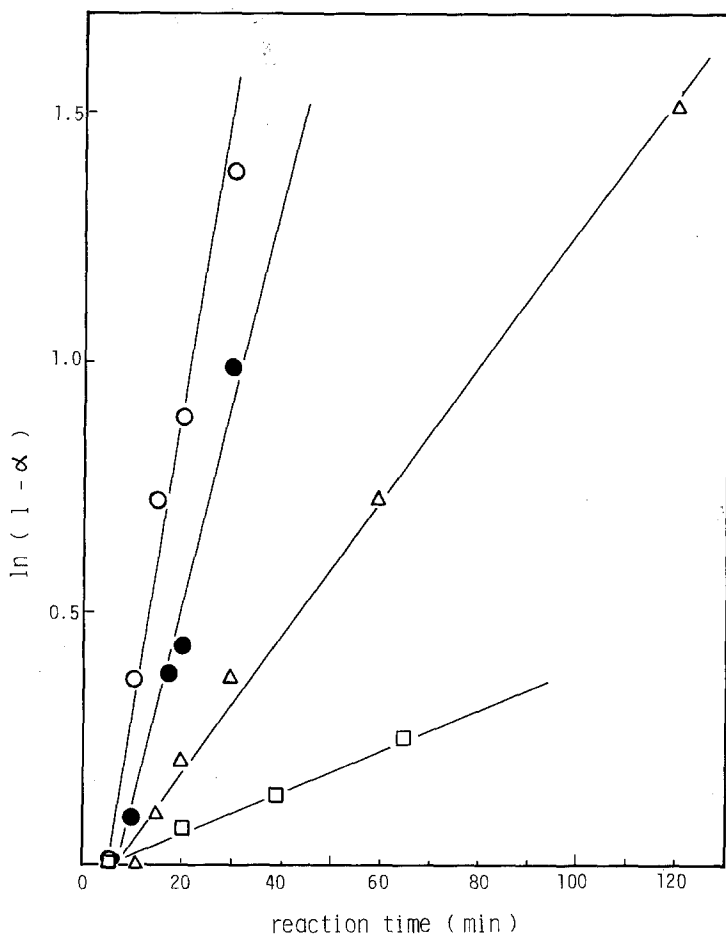
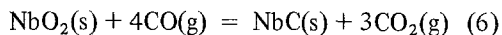
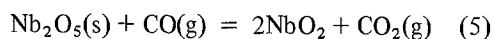


Figure 4 Plots of  $\ln(1 - \alpha)$  against time for the formation of NbC. The point identification is the same as in Fig. 3.

increase the CO partial pressure and thus hinder the progress of reactions 3 and 4 by which NbC is formed. However, the covering actually promotes NbC formation, as shown in Table I, implying that CO could take part in producing NbC as follows,



CO<sub>2</sub> formed in Equations 5 and 6 could be immediately converted to CO by reaction with the carbon abundantly present in the graphite crucible.



Covering the crucible is apparently essential for forcing the formation of NbC to completion at low temperatures, probably because it prevents CO from escaping from the crucible. The mechanism for the participation of CO in the formation of NbC is discussed in detail below, in terms of kinetic considerations.

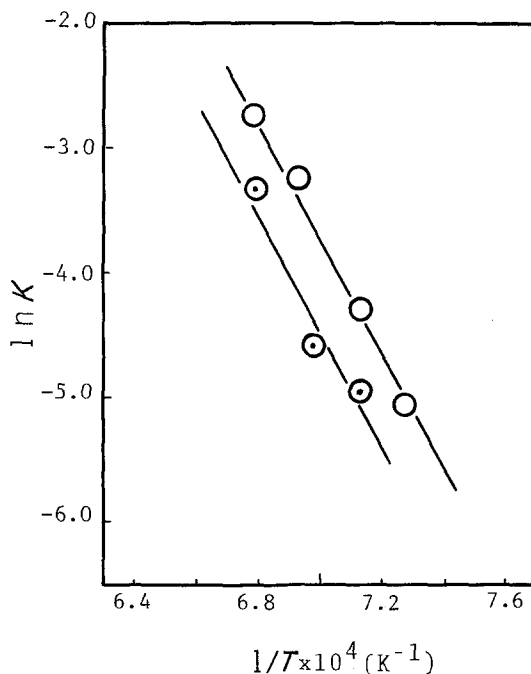


Figure 5 Arrhenius plots of rate constants against reciprocal temperature.  $\circ$ : NbC,  $\square$ : TaC.

TABLE II Experimental results for the formation of TaC by reaction of Ta<sub>2</sub>O<sub>5</sub> with carbon\*

Run number	Reaction vessel	Ratio of C/Ta <sub>2</sub> O <sub>5</sub>	Temperature (°C)	R (%)
1	Covered graphite crucible	7	1260	87
2	Covered graphite crucible	7.5	1260	91
3	Covered graphite crucible	8	1260	100
4	Covered graphite crucible	10	1260	100
5	Graphite crucible	10	1130	17
6	Covered graphite crucible	10	1130	27

\*Source of carbon: active carbon, atmosphere: Ar, time: 60 min.

### 3.1.2. Kinetics of the formation of NbC

Fig. 3 shows the formation rates of NbC by reaction of Nb<sub>2</sub>O<sub>5</sub> with active carbon at 1100 to 1200°C in argon. The reaction was carried out in a covered graphite crucible with a molar ratio of C/Nb<sub>2</sub>O<sub>5</sub> = 10. It is seen that the formation of NbC is complete in 40 or 70 min at 1200 or 1170°C, respectively. The rates appear to be best fitted by first-order reaction kinetics in which nucleation is the rate-determining step [7] as shown in Fig. 4 for the equation,

$$\ln(1 - \alpha) = -kt \quad (8)$$

where  $\alpha$  is the fractional conversion,  $k$  is the constant and  $t$  is time. The intersection of the straight lines at  $\alpha = 0$  after times of 5 to 10 min is due to induction periods of this order, as shown in Fig. 2. SEM (scanning electron microscopy) observations of fully-formed NbC samples showed that the particles are almost the same size and shape as those of the starting Nb<sub>2</sub>O<sub>5</sub> powders, indicating that the formation of NbC occurs on the Nb<sub>2</sub>O<sub>5</sub> particles. That the reaction obeys first-order kinetics (Fig. 4) suggests that in the covered

crucible, nucleation of NbC occurs homogeneously on the Nb<sub>2</sub>O<sub>5</sub> particles. This apparently homogeneous nucleation might be explained by the free surfaces of Nb<sub>2</sub>O<sub>5</sub> particles which have no contact with carbon being covered with an adsorbed layer of CO, which reacts with NbO<sub>2</sub> to form NbC. The very fine particles of Nb<sub>2</sub>O<sub>5</sub> (about 0.2  $\mu$ m) could also provide a physical explanation why a first-order rate law is obeyed. The activation energy for NbC formation was determined to be  $E = 90 \text{ kcal mol}^{-1}$  from the Arrhenius plots of the rate constants (Fig. 5).

### 3.2. Formation of TaC

As described above, the formation of NbC is greatly affected by the reaction vessel and ratio of C/Nb<sub>2</sub>O<sub>5</sub>. The influence of these factors on the formation of TaC by reaction of Ta<sub>2</sub>O<sub>5</sub> with active carbon was also examined in terms of the relative X-ray peak height of TaC, as shown in Table II. The experiments in a graphite crucible with and without the cover (Runs 5 and 6) show that the covering is effective in producing TaC. In a covered crucible, increasing the molar ratio of C/Ta<sub>2</sub>O<sub>5</sub>

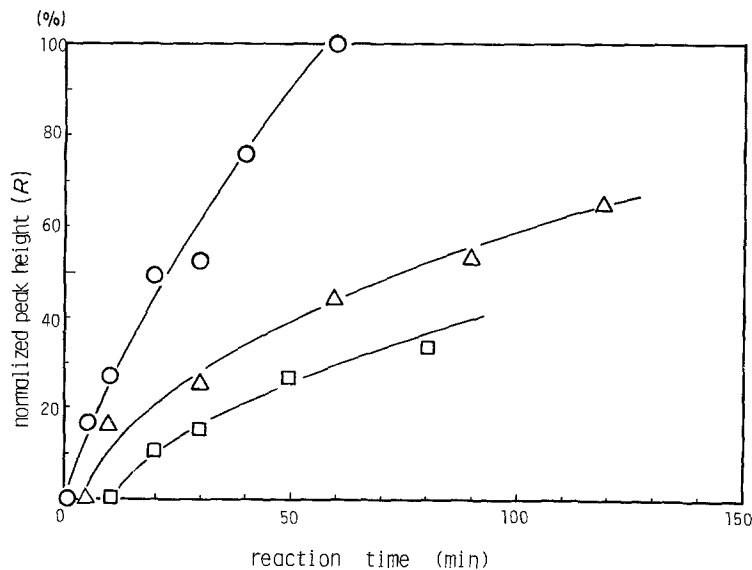


Figure 6 Formation rates of TaC.  $\circ$ : 1225°C,  $\Delta$ : 1160°C,  $\square$ : 1130°C.

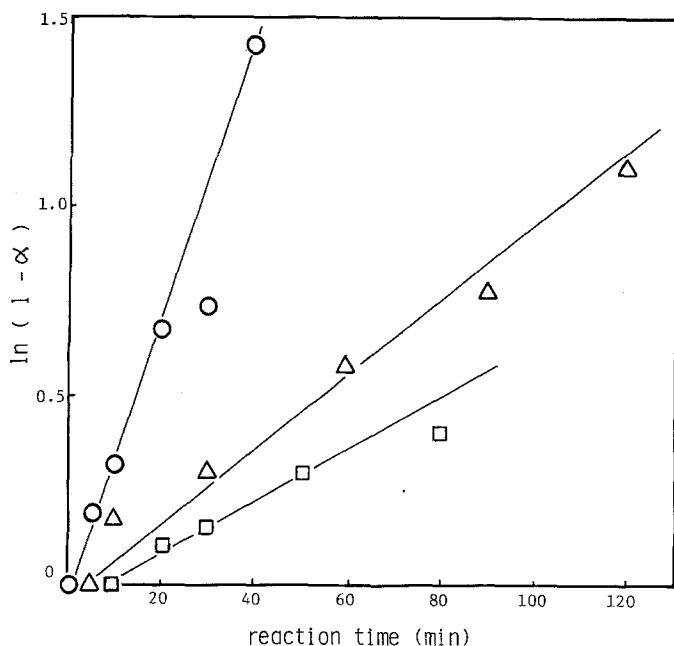


Figure 7 Plots of  $\ln(1 - \alpha)$  against time for the formation of TaC. The point identification is the same as in Fig. 6.

promotes TaC formation; where  $C/Ta_2O_5 = 8$  and 10 (Runs 3 and 4), 100% TaC is produced. Since no formation of any low-tantalum oxide was detected by XRD, the formation of TaC in mixtures of molar ratio  $> 7$  could proceed directly:

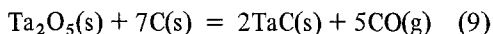


Fig. 6 illustrates the formation rates of TaC by solid-state reaction of  $Ta_2O_5$  with a 10-fold concentration of active carbon, in terms of the relative X-ray peak height. The reaction was carried out in a covered graphite crucible. 100% TaC is seen to form in 60 min at the relatively low temperature of  $1225^\circ C$ . Induction periods of  $t = 5$  to 10 min are observed at  $1130$  and  $1160^\circ C$ , which may represent the time required for the reduction of  $Ta_2O_5$  to produce TaC, without the intermediate formation of low-tantalum oxides. Despite slight deviation, the data appear to be reasonably well fitted by a first-order kinetic equation (Fig. 7). The activation energy was calculated to be  $E = 93 \text{ kcal mol}^{-1}$  from the Arrhenius plots of the rate constants (Fig. 5). Thus, it seems that

the reaction of  $C/Ta_2O_5$  proceeds to form TaC similarly to the formation of NbC: in a covered crucible the homogeneous nucleation of TaC occurs by reaction of  $Ta_2O_5$  both with carbon and with the CO layer on the free surfaces of the  $Ta_2O_5$  particles.

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