



# Production Of NbC from Nb<sub>2</sub>O<sub>5</sub> in a rotating cylinder reactor: Kinetic study of reduction/carburization reactions

F.A.O. Fontes<sup>a</sup>, J.F. de Sousa<sup>b,\*</sup>, C.P. Souza<sup>b</sup>, M.B.D. Bezerra<sup>b</sup>, M. Benachour<sup>c</sup>

<sup>a</sup> Universidade Federal do Rio Grande do Norte, Centro de Tecnologia, Departamento de Engenharia Mecânica, Campus Universitario, 59072-970 Natal, RN, Brazil

<sup>b</sup> Universidade Federal do Rio Grande do Norte, Centro de Tecnologia, Departamento de Engenharia Química, Campus Universitario, 59072-970 Natal, RN, Brazil

<sup>c</sup> Universidade Federal de Pernambuco, Centro de Tecnologia, Departamento de Engenharia Química, Cidade Universitária, 50740-521 Recife, PE, Brazil

## ARTICLE INFO

### Article history:

Received 3 January 2011

Received in revised form

16 September 2011

Accepted 23 September 2011

### Keywords:

Kinetic study

Rotating cylinder reactor

Niobium carbide

Avrami's model

## ABSTRACT

The present work aims at a kinetic model for converting NbO<sub>2</sub> into NbC in the isothermal region of the second reduction/carburization reaction. The model presented for the solid phase was based on the variation of the mass obtained for experiments with reactions interrupted at different times and processed at temperatures of 1148, 1173 and 1223 K. The reaction took place in a rotating cylinder reactor, with rotation velocity of 5 rpm, gas phase flow of  $4.033 \times 10^6$  m<sup>3</sup>/s and initial mass of Nb<sub>2</sub>O<sub>5</sub> 0.004 kg (nominal).

The conversion of NbO<sub>2</sub> was found from the mass balances performed based on the set of stoichiometric equations of the reduction/carburization of Nb<sub>2</sub>O<sub>5</sub> into NbC and used to validate the nucleation model using two parameters (*N*, *M*) which indicate, respectively, the tridimensional growth of the nuclei formed and a fourfold increase in the growth velocity of the nuclei.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

Thermodynamics predicts the synthesis of niobium carbide through solid–solid reactions ( $\text{Nb}_2\text{O}_5 + 7\text{C} \rightarrow 2\text{NbC} + 5\text{C}$ ) to happen under the following conditions: free energy  $\Delta G = 0$  and pressure  $P = 0.1$  MPa at a minimum temperature of  $T = 1228$  K and enthalpy  $\Delta H = +4928$  kJ/kg. Although thermodynamics cannot predict when a reaction will occur, it can predict whether the reaction is truly feasible in practice. Activation energy, diffusion resistances and kinetic considerations about the reaction are the elements that allow the occurrence of a reaction to be predicted. The reduction and carburization of metallic oxides in high temperature rotating ovens have been reported in patents, however applications are still in the development stage. Descriptions of rotating ovens have been cited only in small-scale operations or have focused on theoretical aspects such as heat transfer or material transportation. It is expected that, once perfected, high temperature rotating ovens will produce excellent, consistent, reproducible, and economic carbide powders, which are superior to those currently on the market. In practice, the production of commercial NbC in a fixed bed reactor using a solid–solid reaction occurs at temperatures around 2000 K, Weimer [1].

Different nanostructured carbide synthesis pathways for applications in advanced technologies have been proposed in recent years based on the conversion of various precursors, by means of gas–solid reactions using a flow mixture of CH<sub>4</sub>/H<sub>2</sub>. However, few studies have investigated the kinetics of these transformations. Niobium carbide synthesis through a fixed bed gas–solid reaction from the Nb<sub>2</sub>O<sub>5</sub> precursor was partially investigated by Teixeira da Silva et al. [2]. The kinetics of the first reduction reaction from Nb<sub>2</sub>O<sub>5</sub> to NbO<sub>2</sub> was developed mainly in the temperature ramp zone and agreed with the nucleation model.

The present study shows the results of a kinetic model in converting Nb<sub>2</sub>O<sub>5</sub> to NbC in the isothermal region of the second reduction and the carburization reaction of NbO<sub>2</sub> to NbC. This first part of the model approached the solid phase, obtaining parameters (*M*) and (*N*) of Avrami's nucleation model, Avrami [3,4]. Other model described in the literature (unreacted core model, Levenspiel [5]) was tested for the solid phase but the results did not agree with the ones of this work.

## 2. Materials and methods

The following gases were used: CH<sub>4</sub> (99.99%), special argon (AGA) and synthetic air (White Martins). All were passed through purifiers containing phosphorous pentoxide to remove humidity. The niobium pentoxide Nb<sub>2</sub>O<sub>5</sub> (99.9%) and the niobium carbide NbC (99.46%) were used as supplied by Alfa Aesar (Johnson Matthey Company).

\* Corresponding author. Tel.: +55 84 9981 2989.

E-mail address: [joao@eq.ufrn.br](mailto:joao@eq.ufrn.br) (J.F. de Sousa).

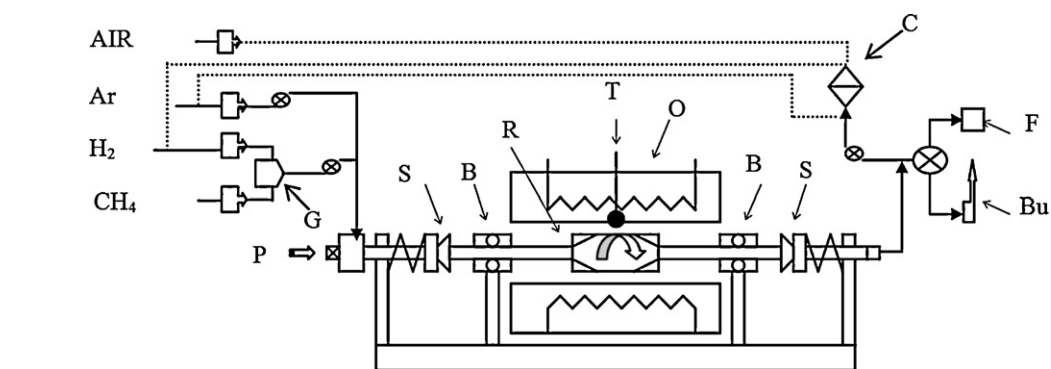
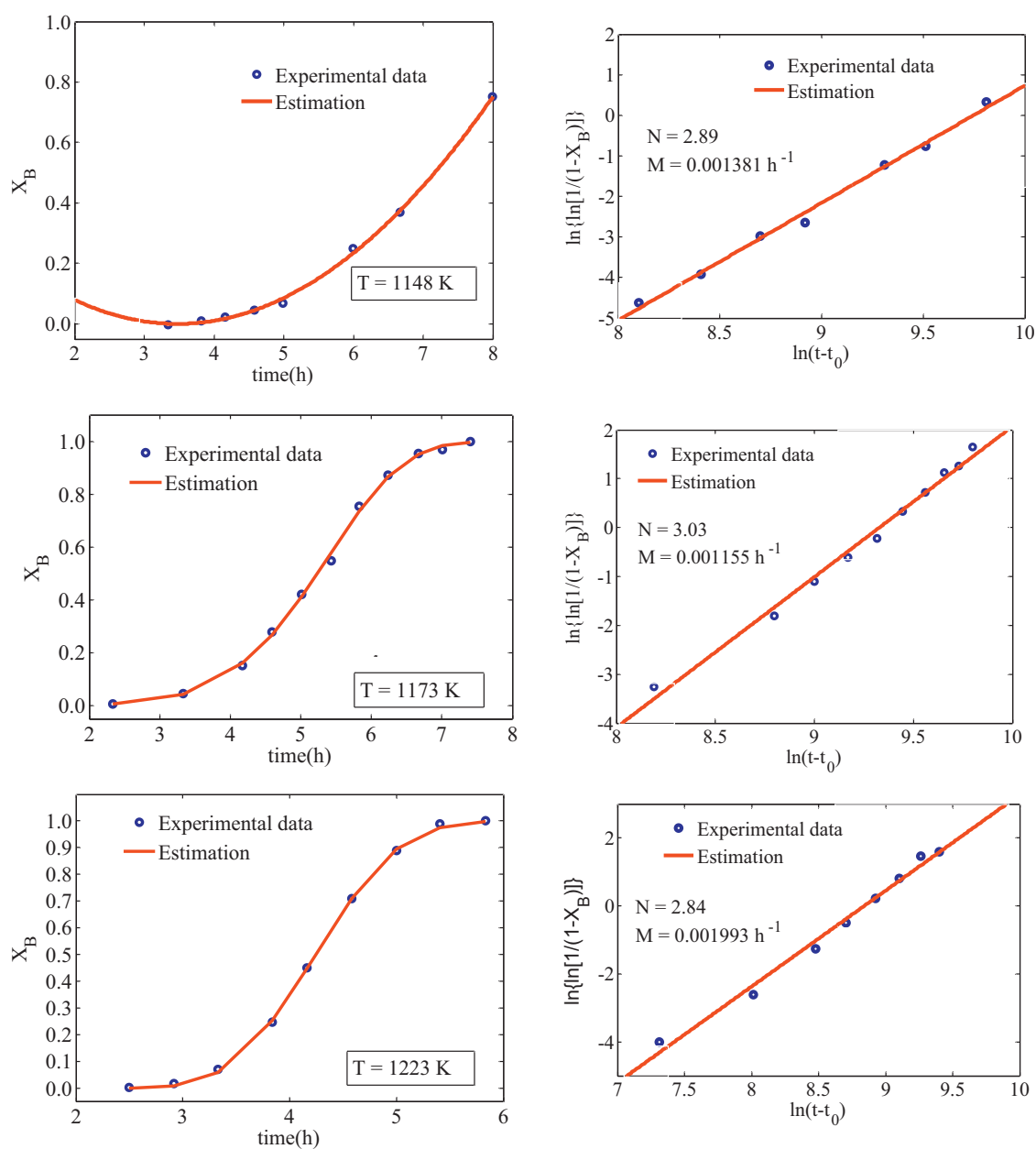


Fig. 1. Experimental device.

Fig. 2. Conversion of  $\text{NbO}_2$  to  $\text{NbC}$  at different temperatures: determination of Kinetic Parameters of Avrami's Model.

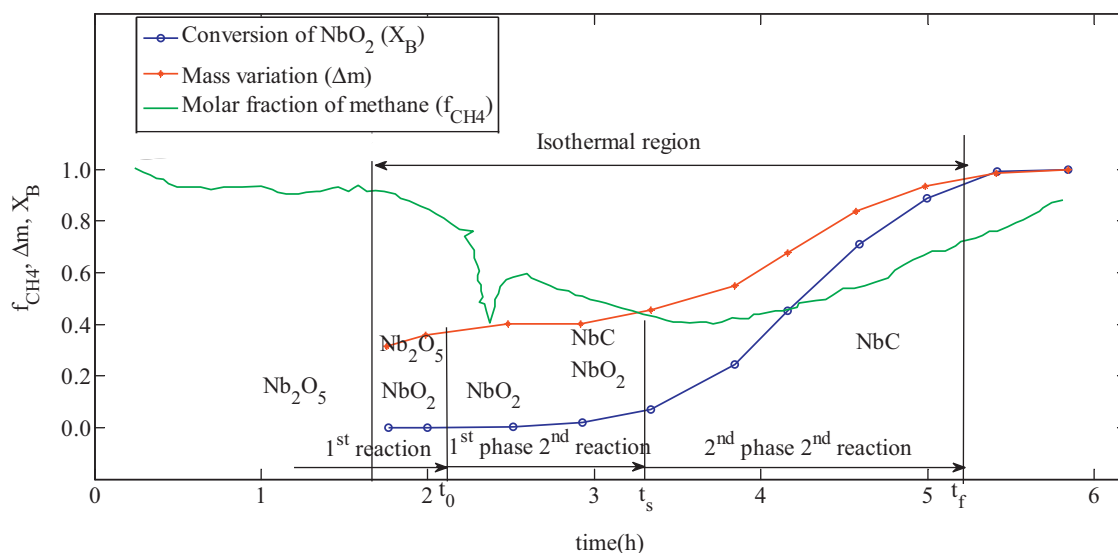


Fig. 3. Dynamic behavior of concentration of methane, mass variation and conversion of NbO<sub>2</sub> at 1223 K.

Fig. 1 shows the device that was designed to carry out the solid–gas reaction:

O – Electric tubular oven; R – Rotating cylinder reactor; B – Bearings; S – Rotating seals; C – Chromatographer; P – Precursor feed; Ar – Argon; H<sub>2</sub> – Hydrogen; CH<sub>4</sub> – Methane; F – Flow meter; Bu – Gas bubbler; T – Thermocoupler; and G – Gas mixer.

The gas distribution unit contained argon for cleaning (Ar) and methane and hydrogen for carbothermic reduction (CH<sub>4</sub>/H<sub>2</sub>) in addition to synthetic air (Air) for an SRI 8610/C Gas Chromatographer coupled with a Flame Ionization Detector (FID) used to monitor the adsorption of methane as well as end of the reaction.

Experimental design was applied to study the kinetics of the carburization reaction of Nb<sub>2</sub>O<sub>5</sub> to NbC carrying out experiments with abrupt interruptions of the reaction at programmed times, according to the procedure described by Montgomery [6].

This step used a localized experiment which investigated temperatures of 1148, 1173, and 1223 K, with the values of the remaining operation parameters fixed at central point values of the response surface methodology (star) used for parameter optimization ( $Q_m$ ) and ( $z$ ) as follows: mass (nominal) of sample  $m_i = 0.004$  kg; heating rate  $\beta = 0.167$  K/s; mixture flow CH<sub>4</sub>–H<sub>2</sub>,  $Q_m = 4 \times 10^{-6}$  m<sup>3</sup>/s; ratio CH<sub>4</sub>/H<sub>2</sub>,  $z = 10\%$  (v/v) and cylinder reactor rotation  $r = 5$  rpm, Fontes [7].

The experiment started with careful weighing of the sample and cleaning of the rotating cylinder reactor chamber. The sample was then fed in and adjustments were made to the following trial parameters: reagent flows, temperature and trial duration. The time intervals when the reactions would be interrupted were defined, and afterwards, according to the results obtained by X-ray diffraction analyses, other points of investigation were carried out. The initial time of the isothermal region ( $t_{is}$ ) varies for each temperature, because the heating rate ( $\beta = 0.167$  K/s) was kept constant at all temperature levels investigated. The trial was initiated when the temperature and reaction time controller/programmer activated the oven. At the end of the established time, the programmer turned the oven off automatically and at that moment, the CH<sub>4</sub>–H<sub>2</sub> flow mixture was removed and substituted by a  $1.6 \times 10^{-6}$  m<sup>3</sup>/s argon flow during cooling until ambient temperature was reached. The reactor continued to rotate to facilitate dissolution of the material. The sample was recovered and care was taken to remove it completely in order not to interfere with the results. One sample in each

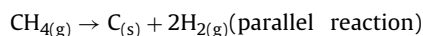
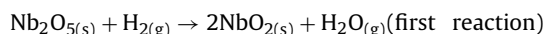
ten trials was repeated to verify the reliability of the experiments. All the samples obtained were characterized by X-ray diffraction to identify the phases present.

In this scientific research, samples were not submitted to the passivation process. However, the passivation process would be carried out if the samples were submitted to gas mixture of helium with 1% O<sub>2</sub>. Moreover, the passivation process does not influence the phase distribution because the phase carbide is already formed and the low oxygen concentration is not able to change the final carbide phase.

### 2.1. Kinetics: solid phase

The present study was based on the set of stoichiometric equations for the carburization of Nb<sub>2</sub>O<sub>5</sub> to NbC in two stages, as presented by Kim et al. [8].

Heterogeneous and consecutive reactions:



In order to validate the model and obtain the parameters  $M$  and  $N$  in accordance with experimental data, it was considered the following hypotheses:

- 1- Isothermal system.
- 2- Solids of invariable size (final size of the particle composed of products equal to the initial size of the NbO<sub>2</sub> particle).
- 3- Piston flow model.
- 4- Solid phase conversion by the nucleation model.
- 5- First-order kinetic model for CH<sub>4</sub>.

### 2.2. Solid phase: general equation



Calling, Nb<sub>2</sub>O<sub>5</sub> = A; NbO<sub>2</sub> = B; NbC = C, thus:  $A \rightarrow 2B \rightarrow 2C$   
Mass balances

Defining for the first reaction the conversion of  $\text{Nb}_2\text{O}_5$  to  $\text{NbO}_2$  by Eq. (1):

$$X_A = \frac{m_i - m(t)}{m_i - m_o} \quad (1)$$

where  $m_i$ : initial sample mass,  $m_o$ : mass at the end of the first reaction =  $m_i f_{c1}^* f_{pd}$ ,  $m_t$ : mass at a time  $t$ , Eq. (2), defined as:

$$m(t) = (n_{\text{Bi}} + 2n_{\text{Ai}})M_B + (n_{\text{Bi}} + 2n_{\text{Ai}})X_B(M_C - M_B) \quad (2)$$

Being  $f_{c1}^* = 2M_B M_A$  (stoichiometric conversion factor of the first reaction),  $f_{pd} = 0.96$  (mass loss factor estimated for loading/unloading),  $n_{\text{Ai}}$ : mol of  $\text{Nb}_2\text{O}_5$  at the beginning,  $n_{\text{Bi}}$ : mol of  $\text{NbO}_2$  at the beginning,  $M_A$ ,  $M_B$ ,  $M_C$ : molecular weight of  $\text{Nb}_2\text{O}_5$  (261.82 g/mol),  $\text{NbO}_2$  (124.91 g/mol) and  $\text{NbC}$  (104.91 g/mol), respectively.

Defining for the second reaction the conversion of  $\text{NbO}_2$  to  $\text{NbC}$  by Eq. (3):

$$X_B = \frac{(m(t) - m_o)}{(m_f - m_o)} \quad (3)$$

where  $m_f = m_o f_{c2}^*$  (mass at the end of the second reaction).

Being  $f_{c2}^* = M_C/M_B$  (stoichiometric conversion factor of the second reaction).

The conversion Eq. (3) of  $\text{NbO}_2$  to  $\text{NbC}$  was used to validate Avrami's nucleation model, Fontes [7].

### 2.3. Validation by Avrami's nucleation model

The next step was to determine the kinetic parameters of Avrami's nucleation model, Avrami [3,4] at temperatures of 1148, 1173 and 1223 K. The solid conversion was determined using the following Eq. (4):

$$X_B = 1 - \exp[-M(t - t_o)^N] \quad (4)$$

where  $M$ : growth rate of nuclei;  $N$ : geometry of nuclei;

For Avrami's model:

$N = 1$ : one-dimensional growth (needle format).

$N = 2$ : two-dimensional growth (disc format).

$N = 3$ : growing three-dimensional format (sphere format).

Fig. 2 shows the experimental values of the conversion of  $\text{NbO}_2$  versus reaction time ( $t$ ) as well as the conversion curves obtained by Avrami's model for 1148, 1173 and 1223 K, respectively. Parameters ( $M$ ) and ( $N$ ) of the model were based on the experimental values at each temperature, the graphs of  $\ln[\ln(1/(1 - X_B))]$  versus  $\ln(t - t_o)$  referent Eq. (4).

## 3. Results and discussion

Fig. 2 shows the results of the experiments performed with reactions interrupted at different times ( $t$ ) for temperatures of 1148, 1173 and 1223 K, respectively and compared with the model (Eq. (4)). The results showed a sigmoidal behavior of the conversion fraction of  $\text{NbO}_2$  ( $X_B$ ) agreed with the nucleation model for the kinetics of the second reaction. It can be observed that the values determined for the exponent ( $N$ ) lie around 3, which shows a tridimensional growth of the sphere-shaped nuclei formed, where all the nuclei are already present at the onset of the second reaction. The growth velocity of these nuclei, represented by the constant ( $M$ ), increases at an approximate proportion of 4:1 between the temperatures of 1148 and 1173 K, as well as between 1173 and 1223 K.

The standard deviations found when determining parameters ( $N$ ) and ( $M$ ) of Avrami's model indicate good agreement between

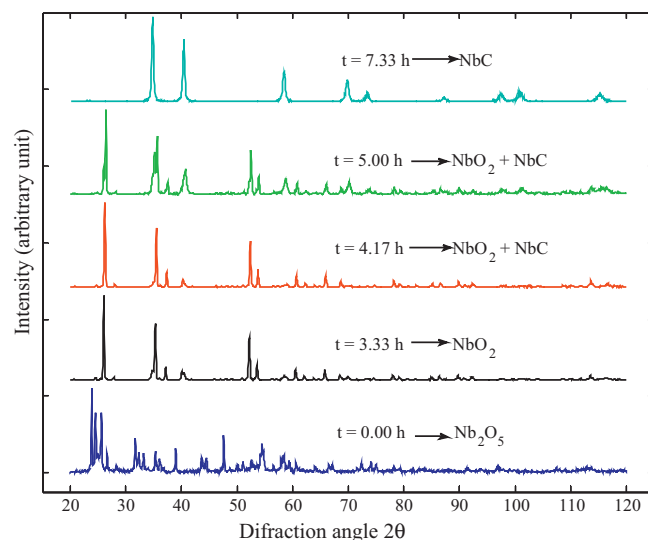


Fig. 4. X-ray diffraction spectra of the different phases formed as a function of reaction time during the formation of  $\text{NbC}$ .  $m_i = 0.004$  kg,  $Q_m = 4.0 \times 10^{-6}$  m<sup>3</sup>/s,  $z = 10\%$ ,  $\beta = 0.167$  K/s,  $r = 0.083$  rps,  $T = 1223$  K.

the experimental values and those expected by the model, as shown in Fig. 2 for the three temperature levels investigated.

Fig. 3 evidences a reduction in the molar fraction of  $\text{CH}_4$ , which could be estimated by Eq. (5), also the curve representing mass variation ( $\Delta m$ ) which was calculated by Eq. (6) and the conversion of  $\text{NbO}_2$  into  $\text{NbC}$  estimated by Eq. (7), as a function of time. The conversion for the model was calculated by Eq. (4).

$$f_{\text{CH}_4} = \frac{C_{\text{CH}_4}}{C_{\text{CH}_4,i}} \quad (5)$$

where  $C_{\text{CH}_4}$ : methane concentration at a time  $t$ , (mol/m<sup>3</sup>),  $C_{\text{CH}_4,i}$ : initial concentration of methane (mol/m<sup>3</sup>)

$$\Delta m = \frac{(m_i - m_t)}{(m_i - m_f)} \quad (6)$$

The conversion  $X_B$  was calculate by Eq. (7)

$$X_B = \frac{(m_o - m(t))M_C}{(M_B - M_C)m_f} \quad (7)$$

It is observed in Fig. 2 a decline in the concentration of methane to the first phase of the second reaction, the attributed to the consumption of this reagent, followed by an increase in this concentration which can be attributed probably to a loss of activity of the solid by deposit carbon in its structure.

The production of  $\text{NbC}$ , being slower, acted as a controlling stage of the process, according to that previously predicted by Teixeira da Silva et al. [2], when they studied the kinetics of the first reaction.

The first reduction reaction of  $\text{Nb}_2\text{O}_5$  to  $\text{NbO}_2$ , according to literature data and those found in the present study, occurred during the heat ramp interval, while the second carburization reaction of  $\text{NbO}_2$  to  $\text{NbC}$  extends itself to the isothermic region for a period that depends on the synthesis conditions.

The induction period preceding the second reaction in which nuclei are formed, starts at the end of the first reaction, where the concentration of methane begins to decrease. The induction lasts until the moment that a new peak appears, indicating a reduction in the concentration of methane at a time  $t_o$ , when the growth of nuclei present starts along with the conversion of  $\text{NbO}_2$  into  $\text{NbC}$ . This behavior is evidenced by the analysis of X-ray diffraction (Fig. 4) made with interruption of the reaction. After the instant when the peak drops in the concentration of methane, it is possible to observe the formation of  $\text{NbC}$ , being characterized then the

beginning of first phase of the second reaction of carburization. The first phase ends when the concentration of methane begins to increase, which corresponds to the beginning of second phase, at time  $t_s$ , it evidences, then, the behavior of consumption of methane in consequence of the deactivation of the solid reagent. The second and final phase of the second reaction is completed at time  $t_f$ , which indicates when the concentration of methane returns to the initial level. The second reaction only occurs when the first is finished, which was evidenced in the X-ray spectra. Fig. 3 shows the behavior at 1223 K only, once at other temperatures the process behaves similarly.

The phases revealed by the characterization of the samples by X-ray diffraction analysis, are illustrated in Fig. 4 for the isotherm ( $T = 1223$  K). Characteristic peaks are observed, indicating the formation of NbC, NbO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> as a function of time. Each diffractogram was obtained as the reaction took place (at different times) to see which compounds were consumed or produced. It can be observed that the formation of NbC begins after 3.3 h of reaction and is fully formed after 5 h, when the chromatogram shows the pure phases.

#### 4. Conclusion

The conversion of NbO<sub>2</sub> to NbC was obtained by means of the fraction of mass variation for the solid phase.

An induction period precedes the second reaction, when the nuclei are formed at the end of the first reaction. The induction period lasts until time  $t_o$ , when growth onset of the nuclei present takes place as well as the conversion of NbO<sub>2</sub> to NbC. The reactions (first and second) occur consecutively, a fact that is made evident by the X-ray diffraction analyses performed on the samples obtained in the interrupted reaction experiments.

The exponent values ( $N = 3$ ) for Avrami's model indicate a tridimensional growth of the nuclei formed and the growth velocity of the nuclei, represented by the constant ( $M$ ), increases of 3.2 times among the temperature levels from 1148 to 1173 K and of 5.5 times among the levels from 1173 to 1223 K.

#### Acknowledgments

Authors would like to thank the Chemical Engineering Graduate Program UFRN Natal, Brazil and the CNPq Scholarship Program for undergraduate students, the LSR UFPB Laboratório de Solidificação Rápida, the LCT EP USP Laboratório de Caracterização Tecnológica and LATMAT UFRN Laboratório de Análise Térmica e Materiais.

#### References

- [1] A.W. Weimer, Carbide Nitride and Boride Materials Synthesis and Processing, Chapman & Hall, New York, 1997.
- [2] V.L.S. Teixeira Da Silva, M. Schmal, S.T. Oyama, Niobium carbide synthesis from niobium oxide: study of the synthesis conditions, kinetics, and solid-state transformation mechanism, *Journal of Solid State Chemistry* (123) (1996) 168–182 (Academic Press).
- [3] M. Avrami, Kinetics of phase change. I: general theory, *Journal of Chemical Physics* (7) (1939) 1103–1112.
- [4] M. Avrami, Kinetics of phase change. II: transformation-time relations for random distribution of nuclei, *Journal of Chemical Physics* (8) (1940) 212–224.
- [5] O. Levenspiel, Engenharia das Reações Químicas, John Wiley & Sons, Inc., Editora Edgard Blucher Ltda, 2000, 3a Edição.
- [6] D.C. Montgomery, Design and Analysis of Experiments, 3rd ed., John Wiley, New York, 1991.
- [7] F.A.O. Fontes, Prototype of rotating cylinder reactor to obtain NbC: reduction and carburization reaction kinetics and performance, 2003, 178f, Tese (Doutorado), Universidade Federal do Rio Grande do Norte, Programa de Pós-Graduação em Engenharia Química, Natal.
- [8] H.S. Kim, G. Bugli, D.G. Mariadassou, Preparation and characterization of niobium carbide and carbonitride, *Journal of Solid State Chemistry* (142) (1999) 100–107.