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In the present work, Fluidized bed reduction of NiO–WO₃ precursors was investigated isothermally at temperatures 973–1273 K. The reaction progress was monitored by analysis of H₂O evolved during the reaction process using a gas chromatograph instrument. A theoretical model based on intrinsic chemical reaction rate constants and thermodynamic equilibria was developed to estimate the apparent reaction rate constant for the reduction reaction. In developing the model, the particles are considered to be in a completely mixed condition and gas flow is described as plug flow. The proposed model is also suitable for scale-up calculations.

The interfacial chemical reaction model was found to fit the experimental results. The apparent activation energy values of the reduction process at different stages were calculated accordingly. The present investigation proved that the fluidized bed technique can be successfully utilized in bulk production of intermetallics containing W and a transition metal (or a composite material) wherein the process conditions would have a strong impact on the particle size of the end product.

KEY WORDS: gas-solid reactions; fluidized-bed; H₂; NiO–WO₃; kinetics; modeling.

1. Introduction

Tungsten alloys have excellent mechanical properties making it suitable material for manufacturing of microstructured tool. Gas-solid reaction route offers unique advantages to the synthesis of W-based alloys, as the process parameters can be well-tailored to suit the product requirements. The products have enough active centers to achieve good chemical bonding between the dispersed material and the matrix during the production process.¹)

The motivation for studying Ni–W–O system is stated earlier.²,³) Several studies have been carried out in the present laboratory to investigate the reduction of transition metal tungstates by hydrogen.⁴–⁷) Ahmed et al.²) studied the reduction kinetics of NiO–WO₃ mixture by hydrogen using thermogravimetric technique. They correlate the activation energy values and molar ratio of Ni/(Ni+W) and revealed that it increases with the increase in Ni/(Ni+W) molar ratio.

Gas-solid reactors employing fluidized beds have wide-spread applications in the metallurgical industries.⁹–¹¹) The fluidized bed reactor have several advantages like non-agglomeration of the particles, excellent mass and heat transfer, temperature uniformity through the bed, excellent thermal efficiency and low investment costs.¹²,¹³) On the laboratory scale, Srinivasan and Sheasby¹⁴) have studied the hydrogen reduction of hematite to magnetite in a fluidized bed and they found that the reaction was controlled by the reaction at the gas-solid interface. Grace¹⁵) has reviewed the work on modeling and simulation of fluidized bed reactors. A few general models have been proposed for gas-solid reactions in fluidized beds. Doheim¹⁶) has developed a mathematical model for iron ore reduction by hydrogen in a multi-stage fluidized bed reactor. The model has been used to predict the gas and solid conversion for the reduction process. Srinivasan and Staffansson¹⁷) studied theoretically the reduction of iron ore by gases containing CO and H₂ in fluidized bed reactor and they developed a kinetic model for the reduction process.

The efficiency and quality of gas-solid fluidized beds are significantly affected by bubbling, slugging and channeling behavior at gas velocities higher or lower than the minimum fluidization velocity (Um). These result in poor gas solid contact and lower mass and heat transfer.¹⁸) A uniform fluidization exists between minimum fluidization velocity and minimum bubbling velocity (Um). The ratio of Um to Umb is known as fluidization index, which gives an indication of the degree of uniformly expanded bed. Davidson and Harrison¹⁹) and Davies and Richardson²⁰) reported that this ratio tends to be relatively high for Geldart Group-A powders and for high density gases. Singh and Roy²¹) reported that powders having average particle size less than 100 μm will expand uniformly without bubble formation over a limited range of gas velocity greater than the minimum fluidization velocity. Fluidization index can vary from unity to
two. They also mentioned that the higher content of fine particles, the higher fluidization index. For laboratory scale fluidized bed reactors, Morales\(^{22}\) reported that the slugging can be avoided when fluidization velocity \((U_f)\) is higher than \(U_{mf}\) by 1 cm/s where a height to diameter ratio is more than unity.

The present study aims at the application of the fluidized bed technique for measuring the gas-solid reaction rates in order to evaluate the feasibility of producing nano-structured alloys using fluidized bed technique. This includes experimental studies as well as the development of a suitable mathematical model in order to interpret the experimental results. The reduction experiments were carried out isothermally using hydrogen at 973–1 273 K. The chemical reaction involved can be represented as

\[
\text{Ni}_x\text{W}_y\text{O}_z \text{ (solid)} + Z \text{ H}_2 = Z \text{ H}_2\text{O} + \text{Ni}_x\text{W}_y \text{ (solid alloy)}
\]

\((1)\)

### 2. Experimental

#### 2.1. Materials

Three different compositions of Ni–W–O were prepared by mixing NiWO\(_4\) with either NiO or WO\(_3\). These oxides were mixed thoroughly in pre-determined proportions and the mixtures were then pressed into pellets (12 mm in diameter and 5 mm in height), heated up to 873 K and kept for 24 hours. The temperature was then raised up to 1 273 K and sintered for 72 hours in an alumina crucible under argon gas. After sintering, the samples could be removed easily and then crushed in an agate mortar before feeding into the fluidized bed reactor. NiWO\(_4\) was used as received without any pretreatment. The phases and microstructure of the produced NiO–WO\(_3\) mixtures were examined by X-Ray diffraction (Siemens D5000 X-Ray diffractometer, Siemens Co., Germany). Scanning electron microscopy (Hitachi SEM S 37000N, Hitachi High-Technologies Corporation, Tokyo, Japan) coupled with electron dispersion spectroscopy analyses were employed to study the topography, grain size and chemical composition of the sintered samples. Fig. 1 shows the SEM images of the studied precursors.

![Fig. 1. SEM images of the studied precursors, where 1, 2 and 3 refer to precursor number 1, 2 and 3, respectively.](image)

#### Table 1. Characterization of studied precursors.

<table>
<thead>
<tr>
<th>Prec. No.</th>
<th>Mixed oxides percentage, wt.%</th>
<th>Ni/(Ni+W) molar ratio as weighed-in amount*</th>
<th>Composition in wt.%</th>
<th>EDS analysis wt.%</th>
<th>Particle size, (\mu m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NiO NiWO(_4) WO(_3)</td>
<td></td>
<td>Ni W Ni W</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>30 70 —</td>
<td>0.7</td>
<td>46.82 53.18</td>
<td>45.22 54.78</td>
<td>1.6</td>
</tr>
<tr>
<td>2</td>
<td>— 100 —</td>
<td>0.5</td>
<td>24.20 75.80</td>
<td>25.28 74.72</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>— 70 30</td>
<td>0.4</td>
<td>16.89 38.11</td>
<td>14.35 85.65</td>
<td>7.0</td>
</tr>
</tbody>
</table>

* Summation of Ni pct. and W pct. were normalized to 100 pct.
Rotameters suitable to the ranges of the gas flow rates and calibrated prior to the experiments were used to monitor the flow rates of the gases through the reactor tube. The off-gases were led to a Shimadzu gas chromatograph (GC), model GC-2014 with TCD detector (Shimadzu Corp., Kyoto, Japan) by means of a stainless steel tube of 5 mm inner diameter. Hydrogen was employed as a carrier gas while, argon was used as the injector gas. The whole off-gas line was wrapped up with heating tape to prevent H\textsubscript{2}O condensation before the gases entered the GC.

Minimum fluidization velocity was determined experimentally by measuring the pressure drop through the powder bed. The total pressure drop in the reactor with and without the powder bed was measured independently. The gas velocity was adjusted at high flow rate and then decreased incrementally to a rate that was significantly low. At each increment of flow rate reduction, the pressure drop across the bed was measured using a U-tube manometer. The net pressure drop was taken as the difference between the two pressure drops ($P_d$ with powder bed - $P_d$ reactor). A typical graph plotting the pressure drop across the bed against the gas velocity is shown in Fig. 4. The minimum fluidization velocity was determined from the sharp change in the pressure drop.

Calculation of $U_{mf}$ at high temperatures is based on fluid dynamic models elaborated for experimental values produced at room temperature ($U^*_{mf}$). It is well known that, upon temperature increase, both density and viscosity of the fluidizing gas will change. $U_{mf}$ can be calculated at higher temperatures according to the following equation.\textsuperscript{24)

$$U_{mf} = U^*_{mf} \frac{\rho_r \mu_r}{\rho_T \mu_T}$$\textsuperscript{(1)}

Where $\rho_r$ and $\mu_r$ and $\rho_T$ and $\mu_T$ stand for the density and viscosity at room temperature and high temperature, respectively. The $U_{mf}$ values obtained at room temperature for different precursors and those estimated at different temperatures as well as $U_f$ are listed in Table 2. The sample mass for each precursor was chosen suitably so that the bed height ($H$)/diameter ($D$) was higher than unity. The typical amounts taken were 6 g sample of prec. 1, 4 g of prec. 2 and 7 g of prec. 3. For the present study, ($U_f - U_{mf}$) was estimated.

**Fig. 2.** Isothermal section from the Ni–W–O phase diagram at 1273 K.

**Fig. 3.** Schematic drawing of the GC connected fluidized bed.

**Fig. 4.** Pressure drop as a function of hydrogen gas flow rate.
to be about 1 cm/s and $H/D$ was higher than unity, leading to a good mixed solid suspension as well as minimizing the elutriation of the finest particles, slugging and bubbles formation.

The sample was allowed to rest on the porous disc in the reactor. The reactor was positioned in the furnace in such a way that the powder bed was at level of 20 mm below the center of the even temperature zone. The sample then was heated up in argon atmosphere and when the desired temperature was reached and stabilized, the argon gas was replaced by hydrogen. The water vapor in the off-gases was monitored by GC. As the reaction progressed, the relative concentration of water, which is resulted from the reduction process, was monitored using the gas chromatograph (GC) in the form of peaks. After the reaction finished, as indicated by the zero $H_2O$ output, the hydrogen gas was replaced by argon and the sample was furnace-cooled.

### 3. Results

The area under the GC peaks ($A_r$) was plotted as a function of time. On the basis of this plot, the integration of $A_r(t)dt$ was normalized to the maximum reduction degree achieved on TGA experiments for the same precursors and the reduced fraction was, thus, calculated backwards. Figure 5 shows the reduction curves obtained the applied precursors. The degree of reduction at given time ($t$) is defined as the ratio of mass loss ($\Delta M$) to the theoretical mass loss ($\Delta M_T$).

$$X = \frac{\Delta M}{\Delta M_T} \tag{2}$$

The value of $X$ can be described as the ratio of area under the curve, at time $t$, $A_r(t)$ to the area at the time when the reaction completed. So, reduced fraction at time $t$ can be expressed as follows;

$$X = \frac{\int_0^t A_r(t)dt}{\int_0^T A_r(t)dt} \tag{3}$$

From the reduction curves, it can be seen that reduction rate significantly increases with the increase of temperature. In precursor 1 curves, it can be seen that about 70% of the reduction is achieved after 1000 s at 973 K while, at 1273 K, the reduction is completed in 300 s. The Ni/(Ni+W) molar ratio seems to have an effect on the reduction rate. It

### Table 2. Summary of fluidization conditions.

<table>
<thead>
<tr>
<th>T, K</th>
<th>Precursor No.1</th>
<th>Precursor No.2</th>
<th>Precursor No.3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$U_{mn}$ cm/s</td>
<td>$U_{mn}$ cm/s</td>
<td>$U_f$ ml/min</td>
</tr>
<tr>
<td>294</td>
<td>3.00</td>
<td>2.17</td>
<td>3.20</td>
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<td>4.79</td>
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<td>5.19</td>
<td>6.19</td>
<td>5.01</td>
</tr>
<tr>
<td>1273</td>
<td>5.33</td>
<td>6.33</td>
<td>5.12</td>
</tr>
</tbody>
</table>

* Measured at room temperature.
** Estimated values at different working temperature.

![Fig. 5. Experimental results for fractional reduction as a function of time.](image-url)
can be seen that the higher Ni/(Ni+W) molar ratio, the higher the reduction rate. At 1273 K, complete reduction of 0.7 Ni/(Ni+W) mixture oxide is achieved after 300 s while for 0.5 Ni/(Ni+W) mixture, this can achieved only after 500 s. For the third precursor, 0.4 Ni/(Ni+W), complete reduction is delayed to 1000 s.

Most of the reduction curves show discontinuity at different fractional reduction values. Earlier studies of kinetics have shown that the reduction of NiO–WO₃ mixtures by hydrogen occurs through three stages in the following sequence;

1. (1st stage) NiO–WO₃ + H₂ → Ni–WO₃ + H₂O ..... (4)
2. (2nd stage) Ni–WO₃ + H₂O → Ni–WO₂ + H₂O ..... (5)
3. (3rd stage) Ni–WO₂ + 2H₂ → Ni–W + 2H₂O ..... (6)

It was reported that the observed discontinuities are related to the change of reaction mechanism according to the above mentioned steps (Eqs. 4–6). The discontinuity becomes less pronounced with decreasing the Ni/(Ni+W) molar ratio.

SEM images of reduced samples having different composition are shown in Fig. 6. These images show the effect of Ni/(Ni+W) molar ratio on the particle size. It is seen that the particle size of the product metallic phase was found to be bigger with the decrease of the Ni/(Ni+W) molar ratio. Agglomeration of the product particles was also observed. The agglomerate was found to be more significant with increasing W content in the precursors. The particle size was found around 1.12, 1.5 and 2.5–3 μm for precursors 1, 2 and 3, respectively.

4. Discussion

4.1. Modeling

Simulation of chemical process involving FB non-ideal reactor, is essential for process design, optimization, control and scale-up. Generally, the gas solid reactions can be considered to have three components, namely:

i. Gas phase mass transfer
ii. Diffusion through the porous reacted shell
iii. Chemical reaction occurring at interfacial surface.

The fluidized bed reactors can be characterized by efficient contact between gas and solid particles and rapid rate mass and heat transfer. Hence, it is reasonable to assume that the mass transfer resistance of gases from the bulk to the particles surface is not significant. As very fine particles have been used in both TG as well as FB, diffusion through the porous reacted shell is also not expected to be significant. As far as the intrinsic chemical reaction rate, expressed for unit mass of particles is considered, it can change depending on the surface area per unit mass of particles. In TG, the amount of H₂ fed per unit mass of Ni–W–O powder is much higher than in FB. Therefore, it is expected that this can result in significant change in overall reduction rates and this is being quantified in the present paper using a model.

In a fluid-solid fluidized bed reactor, one can approximate the fluid flow as plug flow. On the other hand, the solid particles in the bed move in all random directions and hence can be considered to be in a perfectly stirred condition. It is also well-known that the vigorous motion of the solid particles in a fluidized bed will ensure the temperature equalization along the bed. The isothermal characteristic within the bed is one of the most characteristic properties of the fluidized bed reactor. Therefore, if pure hydrogen in injected into a fluidized bed consisting of Ni–W–O particles, the concentration of H₂O in the gas increases along the flow direction. Therefore, the reaction rate diminishes as the gas moves depending on the equilibrium constant for the reaction. This forms the basic premise for the model development.

The model is based on the following assumptions

i. The system is considered to be isothermal (the temperature gradient in fluidized bed unit is negligible in the reaction zone even when reactions involving large heat effects indicating a very high degree of mixing within the bed).
ii. The gas flow is plug flow. The solid particles are well stirred and hence can be considered having homogeneous composition at any instant of time.
iii. The mass transfer resistance for the reaction is small compared to the intrinsic reaction rate.
iv. The particle sizes are small enough that diffusive transport of gas through the product layers particles can be neglected.

With the above assumptions the present model will be considered. The mathematical description of this model is presented along with the results computed using the model.

The fluidized bed system is represented schematically in Fig. 7. It is based on the assumption that at instant time, the hydrogen partial pressure decreases along the flow direction while H₂O concentration increases.

An equation based on this representation can be written as follows:

\[
d(\frac{dn_{H_2O}(z)}{dz}) = A \ R(z) \quad \text{(7)}
\]

Where \( A \) (m²) is the area of cross section of the reactor, \( z \) is axial co-ordinate, \( n \) (mole/sec) is the molar flux of gas through the reactor, \( x_{H_2O} \) is mole fraction of water vapor in
the gas and \( \dot{R} \) (moles/(m\(^3\).sec)) is the generation of water vapor due to chemical reaction.

The term \( \dot{R} \) can be calculated as

\[
\dot{R} = \frac{N_0^f}{AL} k_f \left( x_{H_2} - x_{H_2O} \right) \]

Where \( N_0^f \) is the total number of moles of reducible oxygen in the Ni–W–O powder, \( L \) is the height of the fluidized bed, \( k_f \) is the intrinsic reaction rate constant and \( K_e \) is the equilibrium constant for the reaction. The term \( \frac{N_0^f}{AL} \) refers to the moles of reducible oxygen present per unit volume of the fluidized bed. It should be noted that the intrinsic reaction rate constant and \( K_e \) can be determined from TG experiments, 2) as

\[
\frac{dX_{TG}}{dt} = k_f x_{H_2} \]

where \( X_{TG} \) refers to reduction rate per unit volume of the fluidized bed and \( \dot{R} \) refers to reduction rate per unit volume of the fluidized bed. It should be noted that the intrinsic reaction rate \( k_f \) can be determined from TG experiments, 2) as

\[
N_0^f \frac{dX}{dt} = A \int_0^L \dot{R}(z) dz \]

where \( X \) is the extent of reduction in the fluidized bed. Additionally the following equations need to be solved to simulate the reduction rate

\[
x_{H_2O} + x_{H_2} = 1 \]

\[
\dot{n}_{H_2} = \frac{\dot{R}}{t} \]

\[
z = 0, x_{H_2} = 1.0, x_{H_2O} = 0 \]

where \( \dot{n}_{H_2} \) is the molar flow rate of the hydrogen into the reactor. Since there is no net generation of gas, the molar flow rate of gas will be remaining the same as the input rate throughout the reactor.

In order to solve the above governing equations, consider the reactor being divided into ‘\( n \)’ zones as shown in Fig. 7. For any zone bound by \( z \) and \( z + \Delta z \), one can write discretized equations based on Eqs. (7)–(9) as follows;

\[
\dot{R}(z + \Delta z) = \frac{N_0^f}{AL} k_f \left( x_{H_2} - x_{H_2O} \right) \left( \frac{1}{K_e} \right) \]

These algebraic equations can be solved for a known value of \( k_f \) to determine the value of \( \frac{dX}{dt} \) and vice versa. It is worth mentioning that the size range of the particles and heat of the reaction (evolved or absorbed) are important factors in the overall reduction process since the process is controlled by a chemical reaction. Size ratio of 1.3 (FB/TG of NiWO\(_4\)) were taken into account for the present model. Besides, the temperature in the FB reactor can significantly drop as the furnace may not be able to supply heat fast enough to compensate the endothermic heat. This was verified by inserting a shielded thermocouple into the fluidized powder bed to measure temperature. Difference of about 10 K was found to exist during the reaction course which is considered in the present simulation. With a set of calculated values of rate constants given in Table 3, the model was used to predict

**Table 3.** Summarizes the numerical values used for calculation (for Precursor No.2).

<table>
<thead>
<tr>
<th>Temp., K</th>
<th>( k_f^* ), s(^{-1})</th>
<th>( N_0^f ), mol</th>
<th>( \dot{n}_{H_2}^* ), mol/s</th>
<th>( K_e^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>973</td>
<td>1.36 e-3</td>
<td>4.97 e-3</td>
<td>4.74 e-3</td>
<td>5.23 e-2</td>
</tr>
<tr>
<td>1048</td>
<td>1.76 e-3</td>
<td>6.95 e-3</td>
<td>6.56 e-3</td>
<td>5.22 e-2</td>
</tr>
<tr>
<td>1123</td>
<td>2.45 e-3</td>
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<td>8.22 e-3</td>
<td>5.22 e-2</td>
</tr>
<tr>
<td>1198</td>
<td>2.67 e-3</td>
<td>1.20 e-2</td>
<td>1.11 e-2</td>
<td>5.23 e-2</td>
</tr>
<tr>
<td>1273</td>
<td>3.17 e-3</td>
<td>1.50 e-2</td>
<td>1.39 e-2</td>
<td>5.21 e-2</td>
</tr>
</tbody>
</table>

* Obtained experimentally from TG results.
** Calculated according to reaction thermodynamics and will be applied for all precursors.
the progress of reduction under the experimental conditions.

A comparison of the predicted and obtained data is shown in Fig. 8 and the values are given in Table 4. It is seen that the agreement is good except at low temperatures and the later stages of the reaction indicating the contribution of mass transfer. As it seen from Table 4, the computed reduction rate of NiWO$_4$ by hydrogen based on TG results are in reasonable agreement with the experimental values of fluidized bed technique. For further confirmation, the present model was applied to two more different oxide mixtures viz. 30%NiO&70%NiWO$_4$ and 30%WO$_3$&70%NiWO$_4$. Tables 5 and 6 show the numerical values used for the calculation as well as both the computed and experimental values for the hydrogen reduction of these precursors.

It can be seen that the present model valid for a wide range of compositions. Table 6 shows that the predicted reaction rate constant is quite close to that calculated experimentally. The present model can be also used to “back-calculate” the intrinsic chemical reaction from the experimental rate constant

4.2. Kinetics

As stated previously, under the present experimental conditions, mass transfer is not likely to be the rate controlling step. On the basis of chemically controlled reduction, especially at the initial stages, activation energy of NiO–WO$_3$ mixtures can be calculated using Arrhenius plot of the isothermal reduction rates at different temperatures as fol-

\[ k = A \exp\left(-\frac{E_a}{RT}\right) \]  

(14)

Where; $A$ is the frequency factor, $E_a$ is the apparent activation energy, $R$ is the gas constant and $T$ is the temperature in Kelvin.

Figure 9 shows plot of $(lnk)$ vs the reciprocal of $T$, $K$, for both second and third stages (Eqs. (7)–(8)) of the reduction process. The first stage (Eq. 6) was difficult to distinguish

<table>
<thead>
<tr>
<th>Temp., K</th>
<th>$k_1^*$, s$^{-1}$</th>
<th>$k_2^*$, s$^{-1}$</th>
<th>$k_3^*$, s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>973</td>
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<td>5.38 e-3</td>
<td>1.72 e-3</td>
<td>1.72 e-3</td>
</tr>
</tbody>
</table>

* 1st stage was not possible to determine it Experimentally.

Table 5. A summary of the numerical values used for such calculation.

<table>
<thead>
<tr>
<th>Temp., K</th>
<th>$k_1^*$, s$^{-1}$</th>
<th>$k_2^*$, s$^{-1}$</th>
<th>$k_3^*$, s$^{-1}$</th>
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<td>5.68 e-3</td>
<td>9.09 e-2</td>
<td>5.24 e-4</td>
</tr>
</tbody>
</table>

* Obtained experimentally from TG results.

** The reaction stages could not be distinguished. So, the reaction considered to process through one stage and equilibrium constant calculated based on the whole reaction rate.

<table>
<thead>
<tr>
<th>Temp., K</th>
<th>$k_1^*$, s$^{-1}$</th>
<th>$k_2^*$, s$^{-1}$</th>
<th>$k_3^*$, s$^{-1}$</th>
</tr>
</thead>
<tbody>
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<td>973</td>
<td>1.53 e-3</td>
<td>0.56 e-3</td>
<td>1.19 e-3</td>
</tr>
<tr>
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</tr>
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<td>1.70 e-3</td>
<td>5.12 e-3</td>
</tr>
</tbody>
</table>

* was not possible to determine the rate constant of the first stage Experimentally.

** The reaction stages could not be distinguished. So, the reaction considered to process through one stage and equilibrium constant calculated based on the whole reaction stages.

Fig. 8. Comparison between computed an experimental results for NiWO$_4$. The symbols represent the experimental values while the lines represent the computed results.
since the reduction of NiO is very fast and the shortest sampling feed time for GC was about one minute.

The present results were fitted to equations corresponding to diffusion control model (Eq. 15) and surface chemical reaction control model (Eq. 16) in order to see whether these could explain the experimental results.\(^{28}\)

\[
\frac{1}{1 - \frac{2}{3}x} - \left(1 - x\right)^{\frac{2}{3}} = k' t \quad \text{............... (15)}
\]

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**Fig. 9.** Arrhenius plot of reduction of NiO–WO\(_3\) mixtures.

**Fig. 10.** Application of chemical reaction kinetic model to the Experimental results. a) Prec. 1, 2\(^{nd}\) stage; b) Prec. 1, 3\(^{rd}\) stage; c) Prec. 2, 2\(^{nd}\) stage; d) Prec. 2, 3\(^{rd}\) stage; e) Prec. 3.
5. Conclusion
Fluidized bed reduction of three different NiO–WO₃ precursors were isothermally studied in the temperatures range 973–1273 K. Preliminary experiments were conducted in order to estimate the minimum fluidization velocity for each precursor individually. The produced powders show that the particle size of the reduction product decreased with the increase of Ni/(Ni+W) molar ratio. X-ray diffraction pattern of the products shows slight shift of Ni peaks from the standard one indicating the dissolution of W into Ni.

The experimental results were found fit the surface chemical reaction model. On applying Arrhenius equation, the calculated activation energy values were in agreement with those determined in an earlier thermogravimetric study.

The present work indicates that the fluidization technique can be applied successfully for the production of intermetallics containing W and a transition metal (or a composite material) wherein the process conditions would have a strong impact on the particle size of the end product.

A mathematical model has been developed to describe the overall reaction rate in a fluidized bed. The model was validated using experimental data for the hydrogen reduction of Ni–W–O powders.

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