A Comparative Study on the Mathematic Models for the Ignition of Titanium Alloy in Oxygen-Enriched Environment

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1. Introduction

Metallic materials, in particular those structural materials in application of Aeronautics and Astronautics, are always suffered from the risk of combustion when serviced under some extreme conditions such as high temperature, oxygen-enriched enrichment, and high-speed friction [1–4]. For example, the titanium and its alloys, as the typical light metals, are widely used in aerospace industry. But the combustion of blades made by titanium alloys have occurred several times due to the high-speed friction between the rotor blades and the engine high-pressure compressor, which is known as titanium fire [5,6]. Not only in titanium alloys, the Ni-based and Fe-based alloys, i.e., superalloys and stainless steels, have also been suffered from combustion in oxygen-enriched atmosphere [7–10]. Once the metallic materials burn, heat-release, it is hard to cease the combustion due to their high combustion heat, fairly low thermal conductivity within 20 s. Hence, it is still a challenge for accurately describing the ignition conditions of metals under the extreme conditions, which is of great significance for the safety-use of materials.

At present, there are different mathematic models to describe the critical ignition conditions of metallic materials. The most common model for describing the critical ignition conditions is put forward by Semenov [11,12]. The model assumes that the ignition
even explosion occurs when the heat generation of materials exceeds the heat loss from the materials to the environment. Bolobov and Khaikin et al. [13–15] have proposed that the titanium particle reaches the melting point of the oxide film at which the thickening and cracking of the oxide layer loses its protective properties, the particle will ignition. They assumed that the oxide layer thicken is ignition temperature related, and established the relationship between the oxide layer thickness and ignition temperature of titanium particle based on the Semenov theory. It can be found that the ignition temperature increases with increase in oxide layer thicken, the theoretical relationship corresponds well with the experimental data. Liang et al. [16] have applied Semenov theory into describing the effects of friction coefficient, oxygen concentration, flow velocity on ignition temperature and ignition delay time with relative error of 8.3% between the theoretical calculation and experimental results. However, the Semenov model ignores the temperature gradient within the sample and assumes that the ignition temperature is irrelevant with the size and shape of samples [11,17], therefore it is still a challenge for describing the ignition of components with specific shape in the actual service environment by using the Semenov model.

To overcome the above problems, the Semenov model has been modified by Frank-Kamenetskii. The Frank-Kamenetskii theory has established basing on the assumption that temperature gradient exists within a sample and the heat transfer process follows the Fourier’s law [18,19]. To describe the stationary temperature distribution, a dimensionless parameter is introduced in Frank-Kamenetskii model. This parameter and the boundary conditions contain only one maximum steady-state solution, that is, the ignition criterion of Frank-Kamenetskii model. If the Frank-Kamenetskii parameter is larger than the steady-state solution, ignition will occur [20,21]. This theory model has been used for combustion of coal [22,23], compounds [24,25], batteries [26,27], etc. In recent years, He et al. have predicted the spontaneous ignition conditions of batteries using the Frank-Kamenetskii model [26]. It can be found that the ignition temperature decreases as number of cells increases, and a Frank-Kamenetskii model analysis using these ignition temperature shows a well linear fit between thermal properties and inverse critical ambient temperature. The parameters extracted from the theory are used to verify the laboratory results, which is close to the experimental values. In addition, Bolobov et al. have studied the relationship between the initial temperature of carbon steel and the difference value of the maximum temperature and ignition temperature under different oxygen pressures, and proposed that the ignition mechanism of carbon steel is that the thermal self-acceleration of oxidation reaction of metals under the condition of subcritical self-heating of sample [28]. Although there are some models to describe the critical conditions of materials, the model for describing the critical ignition conditions of bulk metallic materials introduced by promoted ignition test and the parameters determination in the model are still unclear.

In this paper, the mathematic models based on Semenov and Frank-Kamenetskii theory were introduced into describing the effects of size, oxygen concentration, and oxygen pressure on the ignition temperature and critical oxygen pressure of TC17 alloy. Through the determination of the ignition criterion parameters, the ignition temperature of TC17 alloy with different sizes is predicted, and the validity of the criterion is verified.

2. Mathematic Model
2.1. Heat Transfer Model

A steady-state model of heterogeneous combustion of TC17 alloy in the gaseous oxidizer environment is considered as schematically illustrated in Figure 1. TC17 alloy is heated up by convection mechanism and its temperature is raised from initial temperature to its ignition temperature. Once the sample reaches to its ignition temperature, the burning process is started. At this stage, oxygen absorbs to the sample surface and dissociates to the oxygen radicals and diffuses into the sample. Due to the heat liberated by combustion, the sample temperature increases. The combustion phenomenon continues until the sample...
burning time is finished. There is also heat dissipation during combustion. A number of simplifying assumptions are used, as listed below:
1. The ignition ignores the internal thermal resistance of the reaction zone.
2. Constant thermophysical properties for the TC17 alloy are used.
3. Phase transformation of titanium alloys is neglected.

![Figure 1. Heat transfer model of titanium alloy at high temperature.](image)

The heat dissipation in the reaction zone is realized by convection heat transfer between the reaction zone and the environment and the conduction of the sample, ignoring the influence of heat radiation.

Based on the above assumptions and the thermal ignition theory, a heat transfer model for the ignition process of titanium alloy under promoting ignition condition is established, which can be written as follows:

\[
\left. \frac{dQ_i}{dt} \right|_{T=T_0} = Q_g - Q_l
\]

where \( Q_i \) is the internal energy, \( T_0 \) is the ignition temperature. \( Q_g \) is the rate of energy generation, \( Q_l \) is the rate of energy loss.

### 2.2. Ignition Criterion

#### 2.2.1. The Ignition Criterion of Semenov Model

According to the ignition criterion, the ignition of TC17 alloy occurs when the rate of energy generation (\( \dot{Q}_g \)) is equal to the rate of energy loss (\( \dot{Q}_l \)), and the derivation of the energy generation rate and energy loss rate with respect to temperature are equal.

\[
\dot{Q}_g = \dot{Q}_l
\]

\[
\frac{\partial \dot{Q}_g}{\partial T} = \frac{\partial \dot{Q}_l}{\partial T}
\]

In the Semenov model, the rate of energy loss (\( \dot{Q}_l \)) is mainly the rate of change in the convection energy (\( \dot{Q}_a \)). According to the Newton’s law of cooling [29], it can be expressed as:

\[
\dot{Q}_l = \dot{Q}_a = A_s h_B (T - T_\infty)
\]

where \( h_B \) is the heat-transfer coefficient, the \( T_\infty \) is the environment temperature, and \( A_s \) is the surface area of the reaction zone.

The rate of energy generation (\( \dot{Q}_g \)) is composed of the rate of energy imputation by resistance wire (\( \dot{Q}_R \)) and the rate of energy generation by the chemical reaction (\( \dot{Q}_0 \)). It is emphasized that the external input energy is equal to zero (\( \dot{Q}_R = 0 \)) at the ignition moment.
The rate of energy generation due to chemical reaction per unit time on the surface for reaction zone can be represented as:

$$\dot{Q}_g = \dot{Q}_R + \dot{Q}_O = \dot{\omega}_{Ti} A \rho^* r$$  \hspace{1cm} (5)

where $\dot{\omega}_{Ti}$ is the weight gain per unit area per unit time [30], $Q^*$ is the heat of the reaction per unit mass.

The $\dot{\omega}_{Ti}$ is dependent on the reaction model of sample. Here, the chemical adsorption and oxide film thickening model is used in Equation (5).

(a) Chemical absorption model

In the chemical absorption model, $\dot{\omega}_{Ti}$ is the absorption rate of the matrix with oxygen, which can be expressed as follows [31]:

$$\dot{\omega}_{Ti} = k' \exp \left( -\frac{E'}{RT} \right) \frac{\left( C_i P \right)^{n'}}{1 + \alpha'(1 - C_i)^{n'} P}$$  \hspace{1cm} (6)

where $k'$ and $E'$ are the preexponent and activation energy of the rate of oxygen absorption, $n'$ and $\alpha'$ are the reaction order and adsorption coefficient, respectively, $R$ is the molar gas constant, $C_i$ is the oxygen concentration, $P$ is the critical oxygen pressure, and $P_a$ is the atmospheric pressure.

(b) Oxide film thickening model

In the oxide film thickening model, $\dot{\omega}_{Ti}$ is the rate of oxide film thickening. According to the oxidation kinetics of titanium alloys, it is expressed as follows [32]:

$$\dot{\omega}_{Ti} = \frac{d\tau}{dT} = \frac{k'' C_i^{n''}}{\delta^m} \exp \left( -\frac{E''}{RT} \right)$$  \hspace{1cm} (7)

where $\tau$ is the thickness of oxide film, $k''$ and $E''$ are the preexponent and activation energy of oxidation respectively, $C_i = P_i / RT$, $P_i$ is the oxygen partial pressure, and $n''$ is the order of the reaction with respect to the oxidation. The exponent $m$ determines the dependence of oxidation rate on the thickness of the oxide film.

In Semenov chemical absorption model, by arranging to the Equations (2)–(6), ignition occurred when Equations (8) and (9) are satisfied.

$$A \rho^* \rho^* \dot{\omega}_{Ti} \exp \left( -\frac{E'}{RT} \right) \frac{\left( C_i P \right)^{n'}}{1 + \alpha'(1 - C_i)^{n'} P} = A_s h_B (T - T_\infty)$$  \hspace{1cm} (8)

$$A \rho^* \rho^* \dot{\omega}_{Ti} \exp \left( -\frac{E'}{RT} \right) \frac{\left( C_i P \right)^{n'}}{1 + \alpha'(1 - C_i)^{n'} P} \frac{E'}{RT^2} = A_s h_B$$  \hspace{1cm} (9)

Dividing Equation (8) by Equation (9), one obtains:

$$\frac{RT^2}{E'} = (T - T_\infty)$$  \hspace{1cm} (10)

In Semenov oxide film thickening model, by arranging to the Equations (2)–(5) and Equation (7). Ignition occurred when Equations (11) and (12) are satisfied.

$$\rho_{n''} \dot{\omega}_{Ti} \rho_{n''} \left( \frac{P_i}{RT P_a} \right)^{\frac{n'' + n'' - n'' - n''}{n'' + 1}} \left[ \exp \left( -\frac{E'}{RT} \right) \right]^{\frac{m - m''}{m'' + 1}} = A_s h_B (T - T_\infty)$$  \hspace{1cm} (11)
\[
\rho_0 \alpha T_A \frac{m+n''}{m+1} \left\{ \frac{m+n''-n''^2}{m+1} \left( \frac{P_m}{RT_p} \right)^{m+n''-n''^2-m-1} \left( \frac{P_i}{RT_p^2} \right)^{m+n''-n''^2-m-1} \exp \left( -\frac{E''}{RT} \right) \right\}^{\frac{m-n''+1}{m+1}} + \left( \frac{P_i}{RT_p} \right)^{m-n''+1} \frac{m-n''+1}{m+1} \left[ \exp \left( -\frac{E''}{RT} \right) \right]^{\frac{m+n''+1}{m+1}} \exp \left( -\frac{E''}{RT} \right) \exp \left( -\frac{E''}{RT} \right) = A_i h_B
\]

Dividing Equation (11) by Equation (12), one obtains

\[
\frac{m+1}{m-n''+1} \frac{RT^2}{E''} - \frac{m+1}{m-n''+1} \frac{RT^2}{E''} = T - T_\infty
\]

2.2.2. The Ignition Criterion of Frank-Kamenetsii Model

Frank-Kamenetsii model has been widely employed to investigate the characteristics of substance self-heating ignition [20]. The energy conservation of the Frank-Kamenetsii model is shown as follow:

\[
\lambda \nabla^2 T + f \cdot q^\circ \exp \left( -\frac{E}{RT} \right) = c_m \rho_m \frac{dT}{dt}
\]

where \( c_m \) and \( \rho_m \) are the specific heat and density of the TC17 alloy, respectively, \( \lambda \) is the thermal conductively of the TC17 alloy, \( f \) depends on the concentration of reactants at any time. In the here, introducing the chemical adsorption into \( f, f = k \alpha (1 - c_i) \).

Under the steady assumption, Equation (14) can be simplified as:

\[
\lambda \nabla^2 T = -f \cdot q^\circ \exp \left( -\frac{E}{RT} \right)
\]

Since the stationary temperature distribution below the explosion limit is reached, in which case the temperature rise throughout the specimen must be small, a new variable \( (\nu = T - T_0) \) is introduced to be here.

So, the Equation (15) can be rewritten as:

\[
\nabla^2 \nu = -f \cdot \left( \frac{q^\circ}{\lambda} \right) \exp \left( -\frac{E}{RT_0} \right) \exp \left( \frac{E}{RT_0^2} \right)
\]

In order to solve Equation (16), some new variables are introduced to be here, \( \theta = \frac{E}{RT_0^2} \), and \( \eta = \frac{x}{l_m} \) (\( l_m \) is the length of the sample, \( x \) is the distance from the center). So, the Equation (16) can be become:

\[
\nabla^2 \eta = -l_m^2 f \cdot \left[ \frac{q^\circ}{\lambda} \right] \exp \left( \frac{E}{RT_0} \right) \exp \left( \frac{E}{RT_0^2} \right)
\]

The critical conditions are \( \eta = 1, \theta = 0, \) and \( \eta = 0, \frac{d\theta}{d\eta} = 0. \) So, it can be defined the maximum steady-state solution of Equation (16) as a nondimensional parameter \( \delta. \)

\[
\delta = \frac{E l_m^2}{\lambda RT^2} k' \cdot \left( \frac{C_i}{RT_0} \right)^n \left[ 1 + \alpha (1 - C_i)^n P \right] \exp \left( -\frac{E}{RT} \right)
\]

where \( k \) and \( E \) are the preexponent and activation energy, \( n \) and \( \alpha \) are the reaction order and adsorption coefficient. The critical condition of ignition, is of the form \( \delta = const. = \delta_c. \) \( \delta_c \) is only related to the shape and size of the specimen, and the values of \( \delta_c \) can be found in literatures [11,33], which is shown in Equation (19).

\[
\delta_c = 0.84 (1 + 1/(b/a)^2 + 1/(l_m/a)^2)
\]
where \( a, b, l_m \) is the length of three sides.

The values of the thermophysical parameters in Semenov model are presented in Table 1. The values of thermodynamic parameters in Frank-Kamenetskii model are calculated by the quantitative relationship between different factors and the critical conditions of TC17 alloy, as shown in Equations (A1), (A4), and (A7) in Appendix A.

Table 1. The thermophysical parameter of TC17 alloy in Semenov model.

<table>
<thead>
<tr>
<th>Standard Symbol</th>
<th>Dimension</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_a )</td>
<td>MPa</td>
<td>1.00</td>
</tr>
<tr>
<td>( R )</td>
<td>J·mol(^{-1})·K(^{-1})</td>
<td>8.314</td>
</tr>
<tr>
<td>( q_r )</td>
<td>MJ·kg(^{-1})</td>
<td>12.00 [34]</td>
</tr>
<tr>
<td>( \rho_{oxi} )</td>
<td>kg·m(^{-3})</td>
<td>( 4.23 \times 10^3 ) [35]</td>
</tr>
<tr>
<td>( \rho_m )</td>
<td>kg·m(^{-3})</td>
<td>( 4.77 \times 10^3 ) [36]</td>
</tr>
<tr>
<td>( \lambda_m )</td>
<td>W·m(^{-1})·K(^{-1})</td>
<td>15.00 [28]</td>
</tr>
<tr>
<td>( l_m )</td>
<td>m</td>
<td>0.070</td>
</tr>
<tr>
<td>( h_B )</td>
<td>W·m(^{-2})·K(^{-1})</td>
<td>11 [37]</td>
</tr>
<tr>
<td>( n' )</td>
<td></td>
<td>0.50 [31,38]</td>
</tr>
<tr>
<td>( a' )</td>
<td>MPa(^{-0.5})</td>
<td>0.52 [31,38]</td>
</tr>
<tr>
<td>( E' )</td>
<td>kJ·mol(^{-1})</td>
<td>44.50 [31]</td>
</tr>
<tr>
<td>( k' )</td>
<td>kg·m(^{-2})·s(^{-1})</td>
<td>4.20 [31]</td>
</tr>
<tr>
<td>( E'' )</td>
<td>kJ·mol(^{-1})</td>
<td>283.50 [39]</td>
</tr>
<tr>
<td>( m )</td>
<td>-</td>
<td>1.00 or 2.00 [14]</td>
</tr>
<tr>
<td>( n'' )</td>
<td>-</td>
<td>1.00 [14]</td>
</tr>
</tbody>
</table>

3. Experimental

3.1. Materials

The TC17 alloy (Ti-5Al-2Sn-2Zr-4Mn-4Cr) ingots were used for this study, and its composition is listed in Table 2. The specimens used for combustion experiments were cut from the ingots into rectangular with the different sizes. These samples were mechanically polished to make its surface roughness reach 1.0 \( \mu \)m for the promoted ignition test.

Table 2. The phase composition of TC17 alloy.

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>Sn</th>
<th>Mo</th>
<th>Cr</th>
<th>Zr</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>4.5–5.5</td>
<td>1.5–2.5</td>
<td>3.5–4.5</td>
<td>3.5–4.5</td>
<td>1.5–2.5</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

3.2. Experimental Methods

The ignition experiment of TC17 alloy was carried out in the promoted ignition device referring to the standard of ASTM-G124 [40]. The simple diagram of the equipment during the experiment was shown in Figure 2. The polished sample was wound by a copper wire with a 1 mm diameter for ignition. The experimental atmosphere was oxygen enriched or a mixed atmosphere of nitrogen and oxygen. Before the ignition tests, the chamber was pumped to a vacuum of \( 10^{-2} \) Pa, and the gaseous was then pumped into the preset oxygen pressures to ignite the samples. The heating rate in experiment was 25 K/s. The critical oxygen pressure of sample could be obtained, which was defined as the maximum oxygen pressure when five consecutive specimens were non-ignited. The ignition temperature was determined by a thermal imager (MCS640, LUMASENSE TECHNOLOGIES, CA, USA) with an accuracy of \( \pm 5 \) K and a temporal resolution of 60 HZ. The burning probability of sample could be obtained, which was defined as the percentage of the combustion occurs times in five experiments. The physical dimensions of the different number of TC17 alloy were shown in Table 1. According to Equation (19), \( \delta_c \) was calculated and shown in Table 3, which demonstrates that as the increase of the size, and \( \delta_c \) increase.
which are divided into three regions, i.e., absolute non-ignition, possible ignition and absolute ignition. It is emphasized that the oxygen pressure with a burning probability of 0% is the critical oxygen pressure of TC17 alloy. The value of A in Equation (A1) is determined to be 0.0098 from the value of \( l_m \). According to the Equation (A1), the reaction order of the ignition criterion of Frank-Kamenetskii model is fitted to be 1.69 by the plots of \( a \) versus \( P \). Thus, from Figure 3b, it can be seen that the ignition criterion of Frank-Kamenetskii model can better describe the relationship between size of TC17 alloy and oxygen pressure.

### Table 3. The \( \delta_c \) of TC17 alloy with different sizes.

<table>
<thead>
<tr>
<th>( a ) (m)</th>
<th>( b ) (m)</th>
<th>( c ) (m) = ( l_m )</th>
<th>( \delta_c ) (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.001</td>
<td>0.005</td>
<td>1.714</td>
</tr>
<tr>
<td>0.0032</td>
<td>0.0032</td>
<td>0.005</td>
<td>2.024</td>
</tr>
<tr>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>2.520</td>
</tr>
<tr>
<td>0.008</td>
<td>0.008</td>
<td>0.005</td>
<td>3.830</td>
</tr>
<tr>
<td>0.010</td>
<td>0.010</td>
<td>0.005</td>
<td>5.040</td>
</tr>
<tr>
<td>0.012</td>
<td>0.012</td>
<td>0.005</td>
<td>6.518</td>
</tr>
</tbody>
</table>

### 4. Result and Discussion

#### 4.1. Effect of Size on Critical Oxygen Pressure

The effect of sample size on critical oxygen pressure and burning probability in enriched-oxygen environment were shown in Figure 3a. It can be seen that the oxygen pressure increases gradually as the size increases. The burning probability of 0% and 100% constitutes the combustion boundary of TC17 alloy with different sizes in enriched-oxygen environment, which are divided into three regions, i.e., absolute non-ignition, possible ignition and absolute ignition. It is emphasized that the oxygen pressure with a burning probability of 0% is the critical oxygen pressure of TC17 alloy. The value of A in Equation (A1) is determined to be 0.0098 from the value of \( l_m \). According to the Equation (A1), the reaction order of the ignition criterion of Frank-Kamenetskii model is fitted to be 1.69 by the plots of \( a \) versus \( lnP \), as shown by the purple curve in Figure 3b. According to the Equation (10), the critical oxygen pressure is size independent in the Semenov model, which is inconsistent with the experimental data. Thus, from Figure 3b, it can be seen that the ignition criterion of Frank-Kamenetskii model can better describe the relationship between size of TC17 alloy and oxygen pressure.

![Figure 2. The simple diagram of combustion equipment and thermal imager.](image)

![Figure 3. (a) The combustion probability of TC17 alloy with different sizes, (b) The relationship between size and oxygen pressure under different ignition criterion.](image)
4.2. Effect of Oxygen Concentration on Critical Pressure

The effect of oxygen concentration on critical pressure and burning probability are shown in Figure 4a. It can be seen that the critical pressure increases gradually as the oxygen concentration decreases. Similarly, the absolute non-ignition region, possible ignition region and absolute ignition region are divided by the probability of 0% and 100%. According to the Equation (A4), by substituting the value of the reaction order \( n = 1.69 \), the absorption coefficient of the ignition criterion of Frank-Kamenetskii model is fitted to be 4.01 by the plots of \([ (1 - C_i)P ]_n \) versus \( (C_iP)^n \), as shown in the purple curve in Figure 4b. As the comparison, for the ignition criterion of Semenov model, the curve of \([ (1 - C_i)P ]_n \) versus \((C_iP)^n\) of chemical absorption model according to Equation (A2) is shown in the black curve in Figure 4b. The curve of \( \ln C_i \) versus \( \ln P \) of oxide film thickening model according Equation (A3) is shown in insert graph in Figure 4b, which the values of reaction order and absorption coefficient are listed in Table 1. It can be seen from Figure 4b that the ignition criterion of Frank-Kamenetskii model is more consistent with the experimental data of oxygen concentration and critical pressure than that of Semenov model.

![Figure 4. (a) The combustion probability of TC17 alloy with different oxygen concentration, (b) The relationship between oxygen concentration and critical pressure under different ignition criterion.](image)

4.3. Effect of Oxygen Pressure on Ignition Temperature

The effect of oxygen pressure on ignition temperature with a size of 0.0032 m in enriched-oxygen environment is shown in Figure 5a. It can be seen that the oxygen pressure increases gradually from 0.13 MPa to 0.59 MPa as the ignition temperature decreases from 1315.9 K to 967.3 K. According to the Equation (A7), by substituting the value of the reaction order \( n = 1.69 \), the activation energy and preexponent are fitted to be 99.23 kJ·mol\(^{-1}\) and 20,230 kg·m\(^{-2}\)·s\(^{-1}\) respectively by the plots of \( T \) versus \( \ln P \), as shown in the purple curve in Figure 5b. As the comparison, for the ignition criterion of Semenov model, the curves of \( T \) versus \( \ln P \) of chemical absorption model and oxide film thickening model according to Equations (A5) and (A6) are shown in the black and orange curve in Figure 5b, which the values of parameters are listed in Table 1. It can be seen from the different curves that the relationship between the oxygen pressure and ignition temperature is better described by the ignition criterion of Frank-Kamenetskii model.

![Figure 5. (a) The relationship between size and oxygen pressure under different ignition criterion.](image)

According to the fitting results of ignition criterion of Frank-Kamenetskii model, it can be concluded that the values of key parameters in the model are shown in Table 4. As a comparison, the thermodynamic parameters in Semenov model also are listed in Table 4.
4.4. The Prediction of Ignition Temperature

By comparing the fitting results, it is can be seen that the ignition criterion of Frank-Kamenetskii model improves the description of the critical ignition conditions of TC17 alloy. According to the parameters of the fitting in the ignition criterion of Frank-Kamenetskii model, as shown in Table 3, the ignition temperature of TC17 alloy with different sizes under 0.45 MPa oxygen pressure is predicted, as shown in Figure 6. The relative error between the experimental and theoretical values is 3.85%. It can be concluded that the ignition criterion of Frank-Kamenetskii model can efficiently predict the ignition temperature of TC17 alloy with different sizes under a certain oxygen pressure, which verified the validity of the ignition criterion. Through the above results and comparison, Frank-Kamenetskii model and its ignition criterion can better describe the critical ignition condition of titanium alloy.

![Figure 5](image_url)  
Figure 5. (a) The effect of oxygen pressure on ignition temperature of TC17 alloy, (b) The relationship between oxygen pressure and ignition temperature under different ignition criterion.

![Figure 6](image_url)  
Figure 6. The relationship between experimental and theoretical values of ignition temperature and size of TC17 alloy.

Table 4. The values of parameters in the ignition criterion of different models.

<table>
<thead>
<tr>
<th>Model Type</th>
<th>Parameter</th>
<th>Dimension</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frank-Kamenetskii</td>
<td>α</td>
<td>MPa⁻¹.₆⁹</td>
<td>4.01</td>
</tr>
<tr>
<td>Frank-Kamenetskii</td>
<td>n</td>
<td>-</td>
<td>1.69</td>
</tr>
<tr>
<td>Frank-Kamenetskii</td>
<td>E</td>
<td>kJ·mol⁻¹</td>
<td>99.23</td>
</tr>
<tr>
<td>Frank-Kamenetskii</td>
<td>k</td>
<td>kg·m⁻²·s⁻¹</td>
<td>20,230</td>
</tr>
<tr>
<td>Semenov</td>
<td>n'</td>
<td>-</td>
<td>0.50 [31,38]</td>
</tr>
<tr>
<td>Semenov</td>
<td>α'</td>
<td>MPa⁻⁰·₅</td>
<td>0.52 [31,38]</td>
</tr>
<tr>
<td>Semenov</td>
<td>E'</td>
<td>kJ·mol⁻¹</td>
<td>44.50 [31]</td>
</tr>
<tr>
<td>Semenov</td>
<td>k'</td>
<td>kg·m⁻²·s⁻¹</td>
<td>4.20 [31]</td>
</tr>
<tr>
<td>Semenov</td>
<td>E''</td>
<td>kJ·mol⁻¹</td>
<td>283.50 [39]</td>
</tr>
<tr>
<td>Semenov</td>
<td>m</td>
<td>-</td>
<td>1.00 or 2.00 [14]</td>
</tr>
<tr>
<td>Semenov</td>
<td>n''</td>
<td>-</td>
<td>1.00 [14]</td>
</tr>
</tbody>
</table>
Semenov model is based on the assumption that the temperature of a sample is uniform, and the heat exchange between the sample and the environment is all concentrated on the surface of the sample. Through the above theoretical derivation, shown in Equations (10) and (13), the critical condition is size independent in Semenov model. However, the combustion of bulk metallic materials in actual environment is strongly related to internal factors, including sample size, shape, grain boundary area. Therefore, the Semenov model is more suitable for describing power, gas, liquid, etc. It is difficult to accurately and quantitatively describe the combustion behavior and critical ignition conditions of bulk metallic materials.

The assumptions of the Frank-Kamenetski model take into account the temperature gradient in the sample system, which is more in line with the actual bulk materials. Therefore, it describes more factors than Semenov model, including sample size, shape, grain boundary area etc. Through the above results, the ignition temperature of bulk metallic materials can be well predicted by the Frank-Kamenetskii model. Moreover, by introducing the Frank-Kamenetskii parameter, the Frank-Kamenetskii model can not only describe the phenomenon of self-heating ignition of bulk materials, but also can better describe the phenomenon of ignition caused by external energy input such as laser, friction, etc., which could be suitable for describing the critical ignition conditions of bulk metallic materials under actual environment in the fields like aviation, weapons, and aerospace.

5. Conclusions

This paper compared the ignition criterion of Semenov and Frank-Kamenetskii model by introducing into describing the effects of size, oxygen concentration, and oxygen pressure on the ignition temperature and critical oxygen pressure, which determines the ignition model for describing the critical ignition conditions of bulk metallic. The conclusions can be drawn as following:

1. The critical oxygen pressure of TC17 alloy increased with the increase of size, which can be described well by the Frank-Kamenetskii model. The critical oxygen pressure is size independent in the Semenov model (including oxide film thickening), which is inconsistent with the experimental data.

2. The reaction order, absorption coefficient and activation energy of TC17 alloy in the ignition criterion of Frank-Kamenetskii model is determined to be $1.69, 4.01 \text{MPa}^{-1.69}$, and $99.23 \text{kJ mol}^{-1}$ respectively by fitting the criterion model with the relationship between the critical oxygen pressure and size, the critical pressure and oxygen concentration, and the ignition temperature and oxygen pressure.

3. The ignition temperatures of the TC17 alloy with different size are predicted by the ignition criterion of Frank-Kamenetskii model with the relative error within 3.85%, indicating that the Frank-Kamenetskii model can be suitable for describing the critical ignition conditions of bulk metallic rather than the Semenov model.

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Conflicts of Interest: The authors declare no conflict of interest.
Appendix A

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_i$</td>
<td>internal energy, J</td>
</tr>
<tr>
<td>$P_a$</td>
<td>atmosphere pressure, MPa</td>
</tr>
<tr>
<td>$Q_g$</td>
<td>rate of energy generation, J K$^{-1}$</td>
</tr>
<tr>
<td>$Q_l$</td>
<td>rate of energy loss, J K$^{-1}$</td>
</tr>
<tr>
<td>$Q_c$</td>
<td>rate of the convection loss, J K$^{-1}$</td>
</tr>
<tr>
<td>$A_s$</td>
<td>surface area of the reaction zone, m$^2$</td>
</tr>
<tr>
<td>$q_{tr}$</td>
<td>heat of the reaction per unit mass, MJ kg$^{-1}$</td>
</tr>
<tr>
<td>$E'_{av}$</td>
<td>activation energy, kJ·mol$^{-1}$</td>
</tr>
<tr>
<td>$E'$</td>
<td>Preexponent, kg·m$^{-2}$·s$^{-1}$</td>
</tr>
<tr>
<td>$k'$</td>
<td>generation</td>
</tr>
<tr>
<td>$k$</td>
<td>convection</td>
</tr>
<tr>
<td>$n'$</td>
<td>surface</td>
</tr>
<tr>
<td>$n$</td>
<td>reaction order</td>
</tr>
<tr>
<td>$n'_{r}$</td>
<td>reaction order</td>
</tr>
<tr>
<td>$R$</td>
<td>molar gas constant, J·mol$^{-1}$·K$^{-1}$</td>
</tr>
<tr>
<td>$C_i$</td>
<td>oxygen concentration, %</td>
</tr>
<tr>
<td>$\alpha'$</td>
<td>adsorption coefficient, MPa$^{-n}$</td>
</tr>
<tr>
<td>$\delta$</td>
<td>threshold value</td>
</tr>
<tr>
<td>$P_{cr}$</td>
<td>critical oxygen pressure, MPa</td>
</tr>
</tbody>
</table>

Subscripts

- $i$: internal
- $g$: generation
- $d$: dissipation
- $c$: convection
- $s$: surface
- $B$: Boltzmann
- $\infty$: environment
- $r$: reaction
- $m$: TC17 alloy material
- $a$: atmosphere
- $n$: convection energy

Appendix B

1. The relationship between size and critical oxygen pressure

In the ignition criterion of Semenov model, it is obvious that the oxygen pressure is independent of the size according to Equation (10).

In the ignition criterion of Frank-Kamenetski model, the experiment is carried out in oxygen-enriched atmosphere and the oxygen concentration is 100% ($C_i = 1$). It is assumed that the change rate of temperature at the ignition moment is a constant. The relationship between size and oxygen pressure can be obtained by rearranging Equations (15) and (16), and taking the logarithm, as shown in Equation (A1):

$$\ln \frac{P}{P_a} = \frac{1}{n} \ln \left( a^2 + A \right) + \frac{1}{n} \ln B$$

(A1)

where $A = \frac{1.68}{0.33} c^2$, $B = \frac{E'_{av} h_B}{R T^2} k c^2 \exp \left( - \frac{E}{R T} \right)$, which is regarded as constant.

2. The relationship between oxygen concentration and critical pressure

When the $C_i$ is 0–100%, it is assumed that the variation of temperature for the same sample is negligible with different oxygen concentration.

In the ignition criterion of Semenov chemical absorption model, the relationship of oxygen concentration and critical pressure can be obtained by the Equation (8), as shown in Equation (A2).

$$\left( C_i \frac{P}{P_a} \right)^{n'_{r}} = C + C a' \left( 1 - C_i \right) P_{cr}^{n'_{r}}$$

(A2)

where $C = \frac{h_B (T - T_{\infty})}{q_{tr} k' \exp \left( - \frac{E}{R T} \right)}$, which is regarded as constant. $a'$ is the absorption coefficient.
In the ignition criterion of Semenov oxide film thickening model, the relationship of oxygen concentration and critical pressure can be obtained by the Equation (10), as shown in Equation (A3).

\[ \ln \frac{P}{P_a} = -\ln C_i + D \tag{A3} \]

where \( D = \frac{m+1}{n^{m+n''-n''\pi}} \ln \left( \frac{h_\alpha(T-T_\infty)}{\rho_{\text{ox}} q \, k \, m^{n^{m+1}} \exp \left( \frac{E}{RT} \right)} \right) + \ln R \), which is regarded as constant.

For the ignition criterion of Frank-Kamenetskii model, the relationship of oxygen concentration and critical pressure can be obtained by the Equation (15), as shown in Equation (A4).

\[ \left( \frac{C_i}{P_a} \right)^n = F + Fa [1 - C_i] P \tag{A4} \]

where \( F = \frac{\lambda_0 RT^2}{E \ln q \, k \, exp \left( \frac{E}{RT} \right)} \), which is regarded as constant.

3. The relationship between oxygen pressure and ignition temperature

   For the ignition criterion of Semenov model, the experiment is carried out in an oxygen-enriched environment and the oxygen concentration is 100% (\( C_i = 1 \)). The relationship between the oxygen pressure and ignition temperature of TC17 alloy with the same size can be obtained by rearranging Equations (8) and (11), and taking the logarithm, as shown in follows:

   Chemical absorption model:

   \[ \ln \frac{P}{P_a} = -\frac{1}{n} \ln (T - T_\infty) + \frac{M}{T} + N \tag{A5} \]

   where \( M = \frac{E}{n^2 R} \), \( N = \ln \left( \frac{h_\alpha}{q \, k} \right) \), which is regarded as constant.

   Oxide film thickening model:

   \[ \ln \frac{P}{P_a} = \ln T + \frac{U}{T} + V \ln (T - T_\infty) + W \tag{A6} \]

   where \( V = \frac{m+1}{n^{m+n''-n''\pi}}, \quad U = \frac{E}{n^{m+n''-n''\pi}}, \quad W = \frac{m+1}{n^{m+n''-n''\pi}} \ln \left( \frac{h_\alpha}{\rho_{\text{ox}} q \, k \, m^{n^{m+1}}} \right), \) which is regarded as constant.

   Similarly, for the ignition criterion of Frank-Kamenetskii model, according to the Equation (15) and the logarithm law, the relationship between the oxygen pressure and ignition temperature of TC17 alloy with the same size can be obtained in oxygen-enriched environment.

   \[ \ln \frac{P}{P_a} = \frac{2}{n} \ln T + \frac{Y}{T} + Z \tag{A7} \]

   where \( Y = \frac{E}{n^2 R}, \quad Z = \frac{1}{n} \ln \left( \frac{\lambda_0 R^2}{E \ln q \, k \, q} \right), \) which is regarded as constant.

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