Non-isothermal decomposition kinetics of copper azide nanowire array

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Abstract. Copper azide nanowire array (CA-NW) was a new primary explosive with high orientation. Thermal decomposition behaviour of CA-NW was studied to evaluate its thermal safety. Thermal decomposition reaction was observed by DSC and TG-DTG methods. Kissinger’s and Ozawa’s methods were used to obtain the kinetic parameters, such as apparent activation energy (E_a and E_o) and pre-exponential factor (A_k). The mechanism functions of thermal decomposition, self-accelerating decomposition temperature (T_SADT), critical temperature of thermal explosion (T_bpo) were obtained. Results show that for CA-NW, E_a=94.08kJ·mol^{-1}, A_k=8.32×10^7 min^{-1}, E_o=97.09 kJ·mol^{-1}, T_SADT=456.6K, and T_bpo=476.6K.

Keywords: copper azide, nanowire arrays, non-isothermal decomposition, thermal safety

1. Introduction
Copper azide is a kind of primary explosive with excellent performance, because it has the advantages of small input energy, large output energy, green environmental protection and so on [1-3]. However, its application is limited due to its extreme sensitivity to shock and friction [1].

There are two promising ways for copper azide to get practical application [2-8]. One way to do this is to tweak its sensitivity properties by tweaking its nanostructure, and another possible method is to isolate dangerous operations from operators by in-situ reaction.

Different nanostructure of copper, such as copper film, porous copper, copper nanowire and copper nano particulars confined inside CNTs, have been used to in-situ react with hydrazoic gas by our group [9-14]. All of these four methods are MEMS-compatible processing techniques, which can realize the nano-crystallization and in-situ reaction of copper azide and fabrication of the energetic material on a chip.

Because of its highly oriented in one direction, copper azide nanowire arrays (CA-NW) is different in performance compared with other different structure of copper azide. Further research on the relationship between structure and performance is needed. In this paper, research efforts are ongoing to study thermal decomposition behavior of CA-NW. This study can help evaluate the application possibility of CA-NW.

2. Materials and Methods
2.1 Fabrication of CA-NW
CA-NW was prepared according to Ref. [9] and its morphology is shown in Figure 1. As clearly observed in Figure 1, CA-NW is highly ordered in length, approximately 500nm in diameter and 50μm in length, and the surface of copper azide is covered with convex structures. XRD result (Figure 2) confirms that CA-NW possess an orthorhombic structure. Except cuprite azide, there are also a little bit tetragonal cuprous azide and cubic copper diffraction peaks observed, which may be caused by the insufficient reaction time.

![Figure 1. SEM image of CA-NW.](image1)

![Figure 2. XRD pattern of CA-NW.](image2)

2.2 Apparatus and experiment parameters
A STA449F3 Simultaneous Thermal Analyzer (NETZSCH, Germany) was used for DSC experiment, the mass of sample was about 0.2mg. The experiment was carried out under the atmosphere of nitrogen, and the flow rate of nitrogen was 50mL·min⁻¹. The heating rate was 10.0K·min⁻¹.

The TG-DTG experiments were carried out by the same equipment, the mass of sample was about 0.2mg. The experiment was carried out under the atmosphere of nitrogen, and the flow rate of nitrogen was 50mL·min⁻¹. The heating rates were 2.5, 5.0, 10.0, 15.0K·min⁻¹, and the temperature conditions range from room temperature to 533K.

3. Results and Discussion

3.1 Thermal analysis
The DSC curve of CA-NW at a heating rate of 10K·min⁻¹ is shown in Figure 3. The corresponding TG-DTG curve is shown in Figure 4. The results show that CA-NW has a strong exothermic peak in the range of 438K ~ 528K, and the mass loss is about 19.4%. The onset temperature \( T_0 = 452.8\) K, peak temperature \( T_p = 488.8\) K, and ending temperature \( T_e = 516.8\) K, respectively.
Figure 3. DSC curve of CA-NW.

Figure 4. TG-DTG curve of CA-NW.

3.2 Non-isothermal decomposition kinetics of CA-NW

Figure 5 shows the CA-NW’s DSC curves of curves in four different heating rates.

![DSC curve of CA-NW at different heating rates.]

The characteristic values, $T_\infty$, $T_p$, and $T_e$, which were obtained under four different heating rates are listed in Table 1.

The kinetic parameters of exothermic decomposition of CA-NW were obtained by using Kissinger’s method [15] and Ozawa’s method [16], as shown in Equation 1 and Equation 2.
Kissinger’s method:

\[
\ln \left( \frac{\beta_i}{T_p^2} \right) = \ln \left( \frac{A_k R}{E_k} \right) - \frac{E_k}{RT_p}, \quad i = 1, 2, 3, 4
\]  

(1)

Where \( \beta_i \) is heating rate, K\text{-min}\(^{-1}\); \( T_p \) is peak temperature, K; \( E_k \) is apparent activation energy obtained by Kissinger’s method, kJ\text{-mol}\(^{-1}\); \( A_k \) is pre-exponential constant, min\(^{-1}\); \( R \) is ideal gas constant, 8.314 J\text{-K}\(^{-1}\)\text{-mol}\(^{-1}\).

Ozawa’s method:

\[
\lg \beta_i = \lg \left( \frac{A E_o}{R G(\alpha)} \right) - 2.315 - 0.4567 \frac{E_o}{RT_p}, \quad i = 1, 2, 3, 4
\]  

(2)

Where \( E_o \) is apparent activation energy obtained by Ozawa’s method, kJ\text{-mol}\(^{-1}\); \( G(\alpha) \) is kinetic model function.

Table 1 lists the calculated values of kinetic parameters. \( E_k \) is consistent with \( E_o \). The value of \( r_k \) and \( r_o \) (the linear correlation coefficients obtained by Kissinger’s method and Ozawa’s method) are all close to 1.

The calculation formula of \( T_{p0} \) (corresponding to \( \beta \to 0 \)) is shown in Equation 3, and the values is also listed in Table 1.

\[
T_{pi} = T_{p0} + b \beta_i + c \beta_i^2 + d \beta_i^3, \quad i = 1, 2, 3, 4
\]  

(3)

Table 1. Kinetic parameters from the exothermic decomposition reaction for CA-NW at various heating rates.

| \( \beta \) K\text{-min}\(^{-1}\) | \( T_o \) K | \( T_p \) K | \( T_e \) K | \( E_k \) kJ\text{-mol}\(^{-1}\) | \( A_k \) min\(^{-1}\) | \( r_k \) | \( E_o \) kJ\text{-mol}\(^{-1}\) | \( r_o \) | \( T_{p0} \) K |
|---|---|---|---|---|---|---|---|---|---|
| 2.5 | 443.1 | 466.4 | 477.5 | | | | | | |
| 5.0 | 448.5 | 474.9 | 489.6 | 94.08 | 8.32E+7 | 0.99 | 97.09 | 0.99 | 456.6 |
| 10.0 | 452.8 | 488.8 | 516.8 | | | | | | |
| 15.0 | 455.0 | 499.9 | 529.6 | | | | | | |

Fig. 6 shows the temperature vs conversion rate (\( \alpha \)) curve at different heating rates. Figure 7 shows the value of \( E \) calculated at a given conversion rate.

When the conversion rate is between 0.1 to 0.85, the value of \( E_o \) is stably distributed between 101.72 kJ\text{-mol}\(^{-1}\) to 80.91kJ\text{-mol}\(^{-1}\). The average value of \( E_o \) calculated is 92.04kJ\text{-mol}\(^{-1}\). The calculated value corresponds to the values obtained using the two methods mentioned above. So, this value is used in later studies to verify the reliability of other methods.
Figure 7. E vs α for the decomposition reaction of CA-NW at different heating rates by Ozawa’s method.

The linear regression analysis of the corresponding E, A and G (α) (the most probable kinetic model function) from each DSC curve of 41 thermal decomposition reaction mechanism functions was carried out by general integral method, such as General Integral equation [17], Maccallum Tanner equation [18] and Agrawal equation [19], and the most available mechanism functions and the corresponding thermal decomposition kinetic equation were obtained. The reliability of the processing method is judged by comparing the consistency of the processing results of Kissinger’s method and Ozawa’s method, etc.

The most probable kinetic model function is shown in Equation 4:

\[ G(\alpha) = (1-\alpha)[-\ln(1-\alpha)]^{\frac{2}{3}} \]  

(4)

The final reaction mechanism of the integral form, differential form and the corresponding thermal decomposition kinetic equation are shown below:

\[ \frac{d\alpha}{dt} = 3 \times 10^{8.64287} \beta \exp \left( -\frac{97.3765}{RT} \right) (1-\alpha)[-\ln(1-\alpha)]^{\frac{2}{3}} \]  

(5)

\[ [-\ln(1-\alpha)]^{\frac{1}{3}} = 10^{8.64287} \beta \exp \left( -\frac{97.3765}{RT} \right) t \]  

(6)

3.3 Thermal safety assessment

For energetic materials, \( T_{\text{SADT}} \) (self-accelerating decomposition temperature) and \( T_{\text{bpo}} \) (critical temperature of thermal explosion) are two important characteristic parameters, which are used to ensure thermal safety and thus ensure their storage and operation safety.

\( T_{\text{SADT}} \) and \( T_{\text{bpo}} \) can be calculated by Equation 7 and Equation 8 respectively.

\[ T_{\text{bpo}} = \frac{E_K - \sqrt{E_K^2 - 4E_KRT_{\text{bpo}}}}{2R} \]  

(7)

\[ T_{\text{SADT}} = T_{\text{bpo}} - \frac{RT_{\text{bpo}}^2}{E_K} \]  

(8)

For CA-NW, \( T_{\text{bpo}} = 476.6 \text{K} \), and \( T_{\text{SADT}} = 456.6 \text{K} \).

4. Conclusions

CA-NW was a new primary explosive with high orientation. Its thermal decomposition behavior was studied to evaluate its thermal safety. The thermal decomposition reaction was observed by DSC and TG-DTG methods.

(1) The thermal decomposition of CA-NW presents one intensive exothermic process. The kinetic equation of the decomposition process is

\[ \frac{d\alpha}{dt} = 3 \times 10^{8.64287} \beta \exp \left( -\frac{97.3765}{RT} \right) (1-\alpha)[-\ln(1-\alpha)]^{\frac{2}{3}} \]
(2) $T_{SADT}$ and $T_{50}$ are 456.6K and 476.6K, respectively.
(3) Results show that the thermal stability of CA-NW is stable at normal temperature and doesn’t decompose.

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