Determining the Activation Energy of Solid-State Phase Transformation of 1035 Steel from Isoconversional Analysis of DSC Data

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Abstract. The results of solid-state phase transformation kinetics analysis for the steel have been controverted because of the complexity and diversity. In this paper, the activation energy, which represents the energy barrier for austenite to pearlite solid-state phase transformation of 1035 steel, was determined from the nonlinear isoconversional method. The result shown that the activation energy is change with the degree of transformation. Therefore, the nonlinear isoconversional approach maybe a better way to calculate the activation energy of solid-state phase transformation.

Keywords. Kinetics analysis, the activation energy, austenite, pearlite, the nonlinear isoconversional approach.

1. Introduction
The complexity and diversity of solid-state phase transition kinetics for the steel have attracted the attention of many researchers [1-5]. For the solid-state phase transformation kinetics, the model of Kolmogorov-Johnson-Mehl-Avrani (KJMA), which is deduced based on the hypothesis of random distribution and isotropic growth of crystal nucleus, was used extensive [6, 7]. It is often impossible to accurately describe the actual kinetic behavior of solid-state phase transformation, because assumption that the kinetic parameters is constant throughout the phase transformation. To improve the model application in dealing with the actual solid-state phase transformation kinetics, some researchers have been revising the model [8-10].

There are two methods to analysis the phase transformation kinetics based on the KJMA model. On the one hand, the method of Kissinger [11] and Ozawa [12] are one approach to solid-state phase transformation kinetics analysis [13]. This approach has been modified by some researches on account of the assumption condition of this approach does not hold in some cases [14]. On the other hand, the approach, which using the model to fit a single experimental curve directly, was used extensive in solid-state phase transformation kinetics analysis [15]. however, the application of this approach has been debated because of the two aspect in the following: (i) the kinetic parameters determined by this approach is constant for the solid-state phase transformation process; (ii) The fitting process is complex and the phase transformation mechanism is not unique. In conclusion, it is result that these approaches have not been widely used to research the solid-state phase transformation kinetics analysis.

In this paper, the method of nonlinear isoconversional was used to data for the solid-state phase transformation of 1035 steel at different cooling rates. We want to prove that this type of analysis method allows to obtain the activation energy from the curve of differential scanning calorimetry. We, therefore, hope that this paper will be obtain the activation energy of the solid-state phase transformation.
2. Theory
Differential scanning calorimetry (DSC) is a widely used experimental technique for the study of phase transformation kinetics [16]. The kinetics rate equation can be expressed by the following.

\[
\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)f(\alpha) = \frac{1}{\Delta_r H_m} \frac{dH}{dt}
\]

(1)

where \(A\) is the pre-exponential factor, \(E\) is the activation energy of the solid state phase transformation, \(R\) is the gas constant, \(T\) is the temperature, \(\alpha\) is the transformed phase fraction, \(\alpha = 1/\Delta_r H_m \int_0^t dH/dt\), \(f(\alpha)\) is reaction model, \(dH/dt\) is the heat flow, \(\Delta_r H_m\) is the total heat released in the process of phase transformation.

For the non-isothermal conditions, substituting the heating rate \(\beta = dT/dt\) into equation (1):

\[
\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)f(\alpha)
\]

(2)

Based on the equation (2), the advanced isoconversional method can be expressed by the minimum value function [17]:

\[
\sum_{i=1}^n \sum_{j=1}^n \left[ \frac{I(E_{a,i},T_{a,i})}{I(E_{a,j},T_{a,j})} \beta_i \right] = 0
\]

(3)

The nonlinear equation (3) may be used to obtain \(E_{a}\) as a condition of minimum value. For a given value of the degree of transformation, substituting experimental values of \(T_{a}\) and \(\beta\) into equation (3), the activation energy \(E_{a}\) can be obtained by equation (3).

3. Experiment
The experimental samples we have chosen the 1035 steel grain, average particle-size of samples were 3mm in length, 2.5mm in width and 2.5 mm in height, and the mass of sample is 105±8 mg. The chemical composition of the investigated steels (in wt%) is given in table 1. The experimental instrument is the thermal Analyzer, SETSYS Evolution. The experimental temperature range is from ambient to 1600 ℃, and the heating rate and cooling rate is from 0.1 to 100 K/min. The isothermal temperature precision is 0.01 ℃. The weighing capacity is 100 mg with a sensitivity of 0.1 μg. The steel grain was placed in corundum crucible, and heated from room temperature to 1550℃ for ten minutes at a constant heating rate (10 ℃/min) in a flowing atmosphere of nitrogen (20 mL min⁻¹). Subsequently, cooling the sample to the room temperature at the cooling rate. Four cooling rate programs are studied: 10, 20, 30 and 50 ℃/min.

| Chemical composition | C    | Si   | Mn   | P    | S    | Ni   | Cr   | Cu   |
|----------------------|------|------|------|------|------|------|------|------|
| wt%                  | 0.3542 | 0.2170 | 0.6099 | 0.0167 | 0.0157 | 0.0105 | 0.0454 | 0.0125 |

4. Results and Discussion
The DSC cures of the phase transformation of 1035 steel of the temperature range is from 800℃ to 500℃ at different cooling rates is shown in figure 1.
Figure 1. DSC curves for the solid-state phase transformation of 1035 steel at different cooling rates (the temperature range is from 800 °C to 500 °C).

In figure 1, the 40 values of $T_\alpha$ were used to determine the activation energy with $\alpha$ in the range 0.025-1 at different cooling rates. By introducing the $T_\alpha$ into equation (3), the $E_\alpha$ dependence on $\alpha$ is shown in figure 2.

![Figure 2](image-url)

Figure 2. Dependence of the $E_\alpha$ on the $\alpha$ determined by the equation (3).

As seen from figure 2, the relationship of the $E_\alpha$ and the $\alpha$ can be divided into three stages. The first stage, the $E_\alpha$ rises from about 70 kJ/mol at the initial stage to nearly 163 kJ/mol at the 30% degree of transformation. At the second stage, the $E_\alpha$ exhibits a single overall value for the process. Subsequently, it decreases to about 67 kJ/mol near the completion of the reaction. In fact, the phase transformation process of steel is a tangled physical processes. Each of these processes has its own activation energy, and the activation energy is likely to be different [18]. Some authors have been proposed that the activation energy of phase transformation varied with the degree of transformation in previous researches. Therefore, the activation energy determined by this approach may be reveal the complexity of the solid-state phase
transformation of 1035 steel at different cooling rates.

5. Conclusions
The nonlinear isoconversional approach has been used to derive the activation energy from the data for the solid-state phase transformation of 1035 steel at different cooling rates. The activation energy obtained by this approach is generally a function of the degree of transformation. The results may be provided fundamental theory for revealing the complexity of the solid-state phase transformation. Therefore, the nonlinear isoconversional approach is meaningfully applicable to determine the activation energy of solid-state phase transformation.

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