THE ACTIVATION ENERGY DETERMINATION IN NON-ISOTHERMAL CONDITIONS FOR THE SOLID-STATE PHASE TRANSFORMATION OF 1035 STEEL

The activation energy of solid-state phase transformation for the steel has been evaluated by the isoconversional method. It is demonstrated that the linear fitting is a mathematically invalid procedure that generally invalidates the isoconversional method. As an alternative, we apply the advanced isoconversional method that can be used to determine the activation energy of solid-state phase transformation of 1035 steel. The activation energy determined by this method varies with the transformed phase fraction. The variation of the activation energy was interpreted by the nucleation and growth model. It is shown that the advanced isoconversional method can be recommended as a trustworthy way of determining the activation energy of solid-state phase transformation of 1035 steel.

Keywords: steel, the activation energy, solid-state, non-isothermal, phase transformation

INTRODUCTION

The solid-state phase transformation kinetics of the steel have been researched by some authors [1-4]. For the solid-state phase transformation kinetics, the model of KJMA (Kolmogorov-Johnson-Mehl-Avrami) which is deduced based on the assumption of random distribution and isotropic growth of crystal nucleus, was used extensive [5]. It is often impossible to accurately describe the actual kinetic behavior of solid-state phase transformation, because of assumption that the kinetic parameters are constant throughout the phase transformation. In order to improve the applicability of the model in dealing with the actual solid-state phase transformation kinetics, some researchers have been revising the model [6].

The Kissinger [7] method and the isoconversional method [8] are commonly used in determining the activation energy of solid-state phase transformation. The Kissinger method determined the activation energy by using the "peak temperature" of the differential scanning calorimetry (DSC) curve [9]. For the past few years, Vyazovkin [10] has pointed out that this method appears to be generally inapplicable for evaluating the activation energy of the processes that occur on cooling. The use of this method with positive values of the cooling rate may result in erroneous values of the activation energy[11]. For the isoconversional method, some applications of isoconversional methods have been de-

rived to deal with the processes of the solid-state phase transformation during continuous cooling [12]. However, the application of isoconversional method which introduced the temperature integral approximation, has created a new misconception about kinetic analysis of cooling data [13].

From the above, the application of these approaches has been debated because of their limitations. In fact, the solid-state phase transformation generally demonstrate a tangled interplay of various processes such as diffusion, nucleation, growth and impingement of the growing new phase particles [14]. These steps have their own activation energies, which are likely to be different [11]. Therefore, it is very important to find an effective method for handling kinetics data measured on cooling. In this paper, we consider the advanced isoconversional method. This method has been very helpful in kinetics analyses calorimetric data on crystallization of liquid metals [15]. The application of the advanced isoconversional method is illustrated for non-isothermal solid-state phase transformation of 1035 steel.

The method of kinetic analysis

The experimental results of the nonisothermal differential scanning calorimetry(DSC) can be used to calculate the activation energy. The kinetics equation is expressed in the following

$$\frac{d\alpha}{dT} = \frac{1}{\Delta_r H_m} \frac{dH}{dt} = \frac{A}{\beta} \exp(-\frac{E}{RT}) f(\alpha) \qquad (1)$$

where α is the transformed phase fraction, $\alpha = 1/\Delta_r H_m \int_0^t dH/dt$, T is the temperature, dH/dt is the heat flow, $\Delta_r H_m$ is the total heat released in the process

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of phase transformation, A is the pre-exponential factor, β is the cooling rate. E is the activation energy of the solid state phase transformation, R is the gas constant and $f(\alpha)$ is a function that represents the reaction model.

For the isoconversional method, there is a lot of isoconversional method based on the logarithmic expression of equation 1 and the approximations of the temperature integral. In my paper, the advanced isoconversional method has been developed which can be resolved the problem of the approximations of the temperature integral. This method can be represented as a condition of minimum value by the following equation [16]:

$$\phi(E_\alpha) = \sum_{i=1}^{n} \sum_{j\neq i}^{n} \frac{J\left[E_\alpha, T_i(t_\alpha)\right]}{J\left[E_\alpha, T_j(t_\alpha)\right]} \qquad (2)$$

Where $J(E_\alpha, T_{\alpha,i})$ is defined as [11]:

$$J\left[E_\alpha, T_i(t_\alpha)\right] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT_i(t)}\right] dt \qquad (3)$$

The equation 2 can be used to determine the E_α for a given value of α based on the minimizing the function $\phi(E_\alpha)$.

Experimental

As experimental examples, the 1035 steel grain was chosen, particle-size of samples were 3 mm in length, 2,5 mm in width and 2,5 mm in height, and the mass of sample is 105 ± 8mg. The experiments were carried out using a thermal Analyzer, SETSYS Evolution, which is made in Setaram of France. The temperature range is from ambient to 1 600 °C, with heating rate and cooling rate from 0,1 to 100 K/min. The isothermal temperature precision is 0,01 °C. The thermocouple is positioned immediately under the sample. The thermal history is determined by the analyzer controller after a standard calibration procedure under the proper conditions. The weighing capacity is 100 mg with a sensitivity of 0,1 μg. Sample was placed in corundum crucible and heated in a flowing atmosphere of nitrogen (20 mL min^{-1}). For experiments carried out under non-isothermal conditions, the sample was heated from room temperature to 1 550 °C at a constant heating rate (10 K/min). In order to melt completely the sample, the temperature was kept constant for 10 minutes under this temperature. Subsequently, cool the sample to the room temperature at a constant cooling rate. Four cooling rate programs are studied: 10, 20, 30 and 50 K/min.

The activation energy

Figure 1 shows the rate of the transformed phase, determined by the DSC curves at different cooling rates. As seen from figure.1, the temperature of the peak gets lower as the cooling rate increases.

The values of T_α shown in Figure 1 were used for 40 values of α in the range 0.025-1 for four experiments performed at different cooling rates. By introducing the T_α
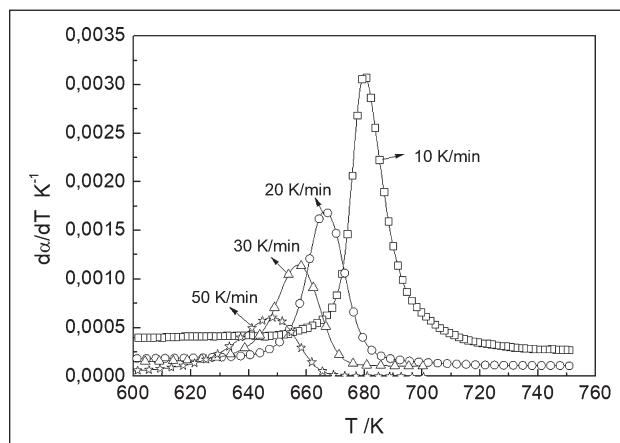

Figure 1 DSC curves for the solid-state phase transformation of 1035 steel at different cooling rates.
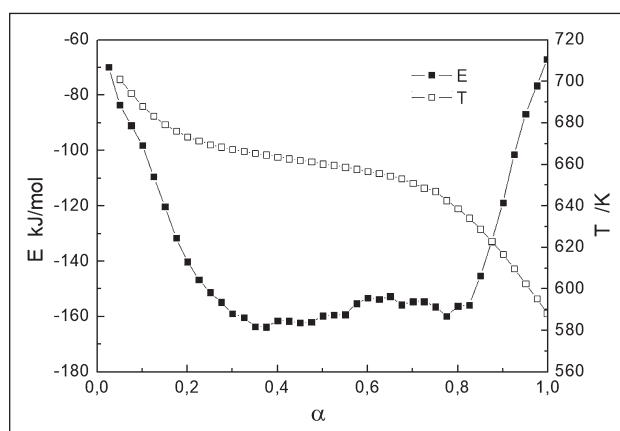

Figure 2 Dependence of the E_α on the α determined by the nonlinear isoconversional method at different cooling rates.

and α into the software of MATLAB. Dependence of E_α on α determined by the software is shown in Figure 2.

As seen from figure 2, the activation energy for the solid-state phase transformation of 1035 steel can be divided into three distinct stages. In the initial stage, the activation energy decreases from about -70 kJ/mol at the low transformed phase fraction to nearly -163 kJ/mol at the 30 % transformed phase fraction. In the second stage, the activation energy exhibits a single overall value at the transformed phase fraction range of 0,3 - 0,8. In the last stage, the activation energy rises from -160 kJ/mol to about -67 kJ/mol near the completion of the reaction. From these phenomena, we can conclud that the investigated solid-state phase transformation kinetics cannot be described as a simple process by a unique set of kinetics parameters.

DISCUSSION

For the solid-state phase transformations process, the overall solid-state phase transformations rate is determined by the nucleation and growth [17]. At the initial stage of reaction, the activation energy of solid-state phase transformations is high; because the necessary

condition for new phase nuclei growth is that the radius of the new phase nuclei is larger than the critical radius. With the temperature of reaction decreasing, the rate of nucleation increases, and the energy barrier of solid-state phase transformations decreases as the transformed phase fraction rises. Once the nucleation process arrives to the end, the new phase nuclei begin to growth. The activation energy basically doesn't vary with the transformed phase fraction. Because the alloy element is conducive to the growth of new phase nuclei, once the temperature drops a certain value, the reaction rate becomes controlled by the diffusion process. At this moment, the activation energy increases with the transformed phase fraction rises because the atomic transition capacity decreases with temperature decrease.

In fact, the process of phase transformation of steel is a tangled interplay of various process such as nucleation of the new phase particles, growth of the new phase particles, atomic diffusion, impingement of the new phase particles, etc [18]. Therefore, the activation energy of phase transformation, which is determined by the activation energies of various processes as well as by the relative contributions of these processes to the total phase transformation rate, is generally a synthetical value, because these processes have their own activation energies, which are likely to be different. In addition, some authors [11] have demonstrated that the solid-state phase transformation kinetics of processes occurring on cooling can be analyzed accurately by the advanced isoconversional method.

CONCLUSIONS

The widely used isoconversional method appears to be generally inapplicable for determining the activation energy of the solid state transformation that occurs on continuous cooling. The activation energy can be evaluated by using the advanced isoconversional method. The application of the advanced isoconversional method to solid state transformation of 1035 steel has obtained the negative values of the activation energy that varies with the transformed phase fraction. The variation of the activation energy can be explained by the nucleation and growth mechanism. In generally, the application of the advanced isoconversional method, which determined the activation energy from the DSC data of the process for the solid state transformation that occur on continuous cooling, can be recommended as a meaningful method.

Acknowledgments

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