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Study of Non-Isothermal Kinetic of Austenite Transformation to Pearlite in CK45 Steel by Friedman Model Free Method

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Abstract

In recent years, many researchers have been done about the kinetics of thermal decomposition processes. In this study, The Friedman model free method were used to study the Non-Isothermal kinetic of Austenite Transformation to Pearlite. DTA method was used at cooling rates of 5, 10 and 20 $^{\circ}\!/\!_{\min}$, under argon atmosphere. Activation energy as a kinetics parameter was determined by using of Friedman model free methods. The results show that the Activation in Friedman model free method are in range of 40.2-43 $^{KJ}\!/\!_{mol}$.

Keywords: Kinetic, Non-Isothermal, Austenite, Pearlite, Friedman model, DTA, Activation Energy.

1. Introduction

Heterogeneous chemical reactions are reactions that the components of reaction are in different phases, these phases that make up the interfaces and usually reactions are performed in interfaces [1]. Reactions are started in Austenite transformation to pearlite from interface of austenite and ferrite. In kinetic study of heterogeneous reactions, is assumed that the equation of rate is also true in the homogeneous gas reactions [2]. In the effect of cooling, in diagram of equilibrium of Iron – Carbon, austenite transformation to pearlite occurs at the temperatures near 727 ° C [3, 4]. In this study, Friedman model free method were used for kinetic of austenite transformation to pearlite in non-isothermal conditions. Using model free methods begin to investigate non-isothermal kinetics from 60 A. D. [5, 6]. In model free methods, is assumed that changing rate of heating the sample, do not change the reaction mechanism and rate reaction is only a function of temperature. Today, determining parameters of kinetics are used by model free methods and the development of equipment [7]. On the base, these methods are obtained from STA or DTA [8]. Freeman, Carroll to calculation parameters of kinetic, use from equation of gases rate, although these equations are correct from the standpoint of mathematical, but from the standpoint of practical are excited some limitations [9]. In addition, Coats and Redfern use from the approximation of temperature function in integral equations, although this approximation has some limitation to convert data into logarithms, but it can be a suitable method for the evaluation initial of the models of kinetic [10]. Ozawa for calculating the activation energy proposes his own method in a fraction of the distinguished converter. In this method, equation 1 is used for calculating activation energy in the various progresses fraction of reaction [11].

$$\ln(\beta_i) = C - \frac{E_\alpha}{RT_{\alpha,i}} \tag{1}$$

In equation 1, C is the constant, $T_{\alpha,i}$ is the temperature in the fraction of distinguished progress, R is the gas constant, β_i is cooling rate and E_α is activation energy in the fraction of reaction progress. For calculating activation energy in each fraction of the distinguished progress (α), changing of $Ln\beta_i$ are drawn vs. $\left(\frac{1}{T_{\alpha,i}}\right)$ and the activation energy is calculated according to slope of the drawn line. Model of fraction of the converter was proposed by Friedman, in this method, is necessary that the experiments are performed at least three different heating rates [5]. In this method, from Equation 2 is used for calculating the activation energy in the various progresses fraction of reaction.

$$\ln\left[\beta_i(\frac{d\alpha}{dT})_\alpha\right] = \ln[Af(\alpha)] - (\frac{E}{RT})_\alpha \tag{2}$$

In this equation, α is the fraction progress of reaction, T is the temperature, R is the gas constant, β_i is the cooling rate, A is the pre-exponential factor, $f(\alpha)$ is the reaction mechanism and E is the activation energy. For calculating the activation energy in each α, changing $\ln\left[\beta_i(\frac{d\alpha}{dT})_\alpha\right]$ is drawn vs. $\left(\frac{1}{T}\right)_\alpha$ and similar Ozawa method, the slope of the drawn lines, will be determined the activation energy. In this study, by using Ozawa and Friedman model free methods, activation energy of austenite transformation to pearlite in CK45 steel was calculated at cooling rates of 5, 10 and 20 $^\circ C/\min$.

2. Method of research

The simple of CK45 steel, with the specified chemical composition in Table 1, was used as basic material. Figure 1 is shown microstructure of the sample which is used. 50 mg samples of the steel was used for the DTA experiments, by apparatus STA 503, for cooling rates of 5, 10 and 20 $^\circ C/\min$, in non-isothermal conditions and under argon atmosphere. The used range for the DTA experiments was 1200 to 650 $^\circ C$.

3. Results and Discussion

Figure 2 is shown the results of the DTA experiments at cooling rates of 5, 10 and 20 $^\circ C/\min$. According to this figure, the start and finish temperatures of austenite transformation to pearlite are calculated and with increasing the cooling rate, the starting temperature of transformation is reduced from 883 to 679 $^\circ C$. For calculating the fraction progress of reaction, the area under peak of DTA curve calculated at any moment and is divided on the area of peak total. Figure 3 shows, the fraction progress of reaction vs. time at different cooling rates. In this Method, not only parameter of time but also temperature is important, values of the fraction progress of reaction and the transformation temperatures were calculated at different cooling rates that are specified in Table 2.

As explained in Equation 1, for Calculating activation energy in each fraction of progress should be drawn changing of $Ln\beta_i$ vs. $\left(\frac{1}{T_{\alpha,i}}\right)$. Table 3 shows the values of $\left(\frac{1}{T_{\alpha,i}}\right)$ for the fraction progress of reaction in various cooling rates. This information has been calculated by using available information in Figure 3. On this base, with increasing the fraction progress of reaction, reduced activation energy partially and in addition to Kinetic barriers that exist in the early stages of transformation, it is justified. It is important that the calculated values of activation energy is the apparent activation energy of transformation and can be included stages of nucleation and growth. Different reports and models in the cases of kinetic of austenite transformation to pearlite have been published But the numerical values is not registered for the activation energy of this transformation [13-17]. It is considered that the mathematical model of Friedman's method (Equation 2) is almost the same as Ozawa method, but in Friedman's method, rate of transformation be calculated with changing of temperature in the fraction progress of reaction $(\left[(\frac{d\alpha}{dT})_\alpha\right])$, be multiplied in the cooling rate. Calculating rate of transformation vs. temperature obtain with the numerical method and according to the calculated values of α from DTA data. Table 4 shows the values of $\ln\left[\beta_i(\frac{d\alpha}{dT})_\alpha\right]$ in the fraction progress of reaction and for different cooling rates and the corresponding temperature. Regarding to Table 4, with increasing the fraction progress of reaction, the values of $\frac{d\alpha}{dT}$ increase and also with increasing the fraction progress of reaction, temperature decrease, the increasing $\frac{d\alpha}{dT}$ can be reasonably justified, Although reduction of temperature can reduce the diffusion carbon and rates transformation But in this conditions the reduction of temperature cannot impress diffusion and austenite rates transformation to pearlite. Figure 4 shows, changing $\ln\left[\beta_i(\frac{d\alpha}{dT})_\alpha\right]$ vs. $\left(\frac{1}{T}\right)$ in the fraction progress of reaction. In this case, the lines which are drawn are not with a difference slope, so the expectation is that the values of activation energy which obtained from the Friedman method does not change so much with the progress of reaction. Table 5 shows the values of activation energy for the austenite transformation to pearlite in the fraction progresses of reaction by using the Friedman model and the existing lines which are calculated in Figure 4. From figure 4 can be comprehend that by the progress of transformation and the increase in the fraction progress of reaction, The activation energy has a minor fluctuation and change from 43 to 40.2 KJ/mol. The obtained information from this method can boost this point that the calculated values of apparent activation energy are largely close to the true value. It should be noted that the obtained values for the activation energy of this method is not justified on a particular model. However, according to Friedman's equation can multiply A in $f(\alpha)$, but don't express the model and the reaction mechanism and for calculating the pre-exponential factor of the Friedman model, is necessary to consider $f(\alpha)$.

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Table 1. Chemical composition of CK45 steel used in this study

%Mn	%S	%P	%Si	%C	steel Heat treatment
0.5-0.8	<0.03	0.35	<0.4	0.42-0.5	CK45

Table 2. Values of the fraction progress of reaction at different cooling rates

fraction progress of reaction	$5\,{}^{C}\!/_{\min}$	$10\,{}^{C}\!/_{\min}$	$20\,{}^{C}\!/_{\min}$
	$T(^\circ C)$	$T(^\circ C)$	$T(^\circ C)$
0.0	883	886	679
0.1	879	882	675
0.2	877	881	672
0.3	876	880	672
0.4	875	879	670
0.5	875	878	669
0.6	874	877	668
0.7	873	876	667
0.8	872	874	666
0.9	871	872	665
1	867	867	662

Table 3. The calculated values by the Ozawa method at different cooling rates

Fraction progress of reaction	$\beta = 5, (Ln\beta_i = 1.609)$ $\left(\frac{1}{T}\right)_\alpha$	$\beta = 10, (Ln\beta_i = 2.302)$ $\left(\frac{1}{T}\right)_\alpha$	$\beta = 20, (Ln\beta_i = 3)$ $\left(\frac{1}{T}\right)_\alpha$
0.1	0.0008679	0.0008654	0.0001054
0.2	0.0008688	0.0008663	0.0001057
0.3	0.0008696	0.0008671	0.0001025
0.4	0.0008704	0.0008679	0.0001060
0.5	0.0008704	0.0008679	0.0001060
0.6	0.0008713	0.0008688	0.0001062
0.7	0.0008721	0.0008696	0.0001063
0.8	0.0008729	0.0008713	0.0001064
0.9	0.0008738	0.0008729	0.0001065

Table4. The calculated values related to Friedman methods at different cooling rates

fraction progress of reaction	$\beta = 5$		$\beta = 10$		$\beta = 20$	
	$Ln\left(\beta_i \times \frac{d\alpha}{dT}\right)_\alpha$	$\left(\frac{1}{T}\right)_\alpha$	$Ln\left(\beta_i \times \frac{d\alpha}{dT}\right)_\alpha$	$\left(\frac{1}{T}\right)_\alpha$	$Ln\left(\beta_i \times \frac{d\alpha}{dT}\right)_\alpha$	$\left(\frac{1}{T}\right)_\alpha$
0.1	-7.34	0.0008679	-6.64	0.0008654	-6.00	0.0001054
0.2	-6.75	0.0008688	-6.06	0.0008663	-5.30	0.0001057
0.3	-6.33	0.0008696	-5.67	0.0008671	-5.00	0.0001025
0.4	-6.05	0.0008704	-5.31	0.0008679	-4.70	0.0001060
0.5	-5.81	0.0008704	-5.13	0.0008679	-4.40	0.0001060
0.6	-5.64	0.0008713	-4.98	0.0008688	-4.30	0.0001062
0.7	-5.49	0.0008721	-4.81	0.0008696	-4.10	0.0001063
0.8	-5.36	0.0008729	-4.69	0.0008713	-4.00	0.0001064
0.9	-5.25	0.0008738	-4.56	0.0008729	-3.90	0.0001065

Table 5. The values of activation energy for the austenite transformation to pearlite in the obtained fraction progress of reaction by Friedman method

Fraction progress of reaction	Activation Energy(J/mol)
0.1	42160
0.2	42600
0.3	41686
0.4	40297
0.5	43099
0.6	41337
0.7	41744
0.8	40738
0.9	41162

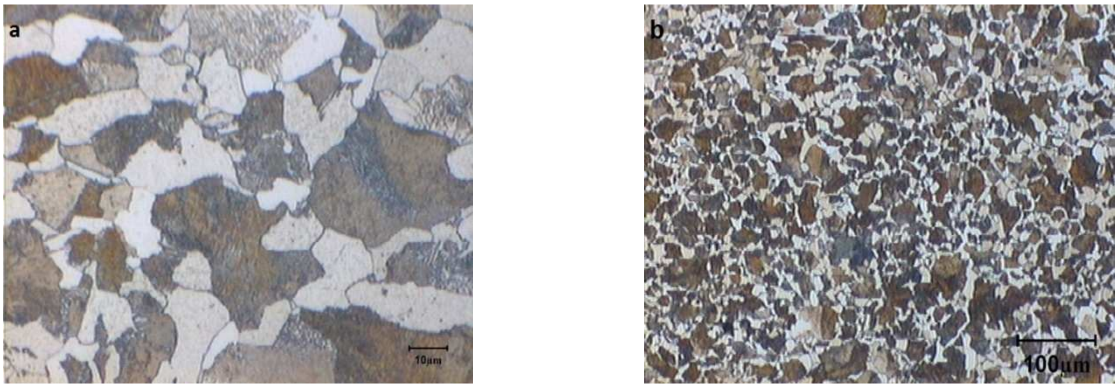
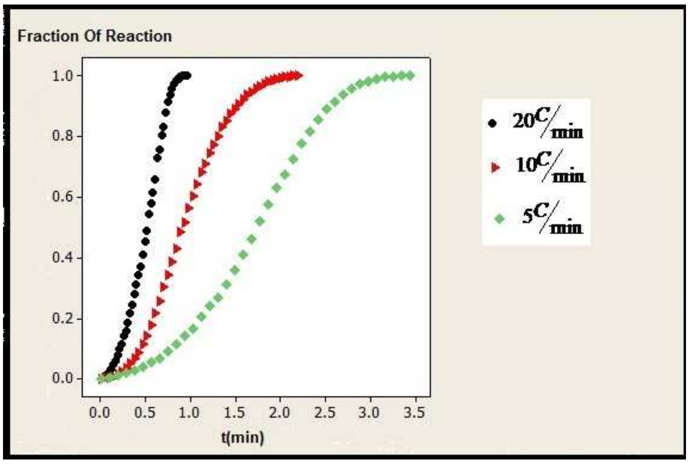


Figure 1. Microstructure austenite transformation to pearlite of CK45 steel a) 500X b) 100X



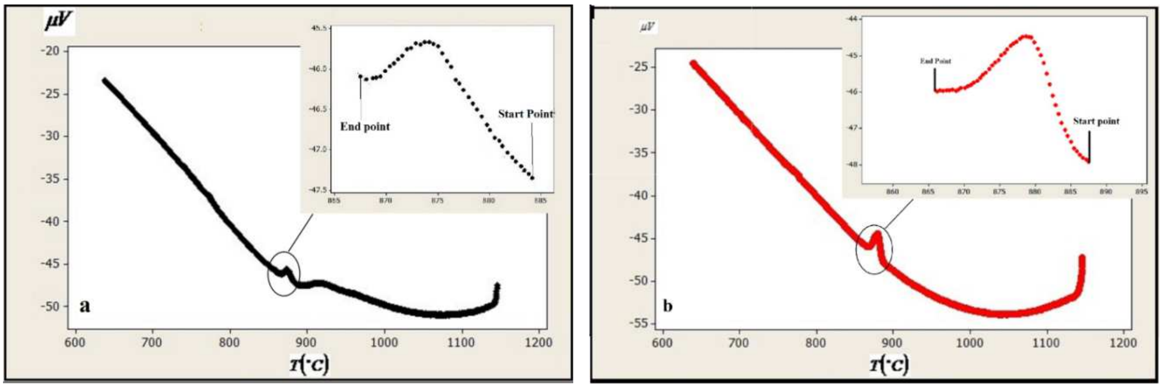


Figure 2. Used peaks to calculate the fraction progress of reaction of austenite transformation to pearlite in the cooling rates (a) 5, (b) 10 and (c) 20 $^{\circ}C/\min$

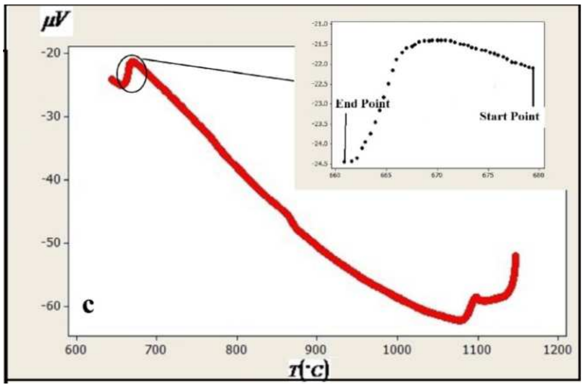


Figure 3. The fraction progress of reaction vs. time

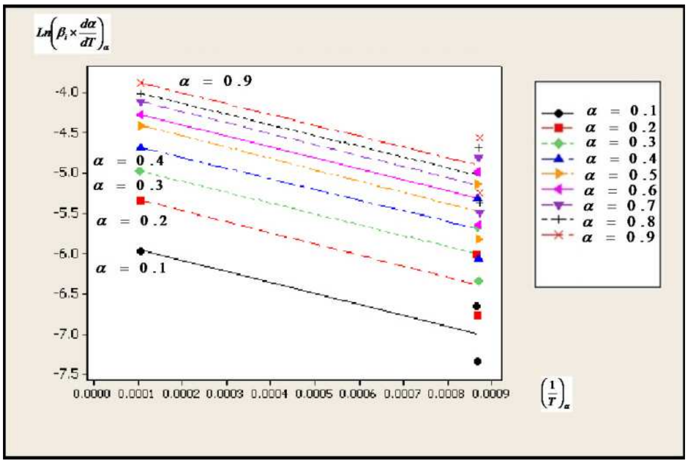


Figure 4. Curves $Ln\left(\beta_i \times \frac{d\alpha}{dT}\right)_\alpha$ vs. $\left(\frac{1}{T}\right)_\alpha$ in the fraction progress of reaction 0.1-0.9