

Research on high temperature corrosion of heating surface of straw boiler

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Abstract. In order to study the high temperature corrosion on straw boiler heating surface, the first is experiment with corrosion environment simulation, the second is linear fit which base on the data from corrosion environment simulation test, it determines the kinetic model function and kinetic triplet parameters. The last is kinetic analysis to obtain the comparison of corrosion resistances. After the comparison between the results of experiment and analysis, it obtains the two are same and verifies the rule of corrosion resistances.

Keywords: High temperature corrosion, linear fit, kinetic analysis, straw boiler

1 Introduction

Thermal analysis kinetics is an emerging discipline, its research purpose is quantitative characterization of the reaction process, it determines the mechanism function of the reaction process and obtains the kinetic reaction parameter and specific reaction rate, it provides the scientific basis for stability rating, acceptable life of various materials, quantitative description of reaction rate and the deduction of reaction mechanism. It is necessary to study the high temperature corrosion on biomass-boiler heating surface.

2 Buildup of corrosion dynamics model

Generally, common solid reaction equation can be expressed as:



Its reaction rate equation is expressed as:

The differential form:
$$\frac{d\alpha}{dt} = kf(\alpha) \quad (2)$$

The integrated form:
$$G(\alpha) = kt \quad (3)$$

In the formula: α is the scores of material A has reacted; t is the reaction time; k is the reaction ratio constant; $f(\alpha)$ is the differential expression of reaction mechanism function; $G(\alpha)$ is the integral expression of reaction mechanism function.

As the $f(\alpha)$ and $G(\alpha)$ are the differential form and the integrated form, their relationship is:

$$f(\alpha) = \frac{1}{G'(\alpha)} = \frac{1}{d[G(\alpha)]/d\alpha} \quad (4)$$

That is:

$$G(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)} d\alpha \quad (5)$$

Reaction rate constant k is an important dimensionless constant which reflect the reaction ratio, it has close relation with the temperature. Most of the relations between it and temperature are the empirical formula, The most common is the expression that Arrhenius suggested:

$$k(T) = A \exp(-E/RT) \quad (6)$$

In the formula: A is pre-exponential factors; E is reaction activation energy; T is absolute temperature; R is plats gas constant.

The reaction rate equation can be expressed as:

$$\frac{d\alpha}{dt} = k(T) f(\alpha) = A \exp(-E/RT) f(\alpha) \quad (7)$$

$$G(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)} d\alpha = \int_0^\alpha A \exp(-E/RT) dt \quad (8)$$

This test is the corrosion test of four specimens reaction in four temperature, but the whole test process proceed in the condition of constant temperature, it belong to the fixed temperature corrosion process. Therefore, it adopts the heterogeneous reaction dynamics equation model in the condition of constant temperature. The varying pattern of corrosion weight per unit area ΔW is defined as $G(\alpha)$, so the derivative to corrosion time t is the corrosion rate of weight gain, it can be represented by the reaction rate k , and obtains the heterogeneous reaction dynamics equation in the condition of constant temperature.

4 The determination of corrosion reaction mechanism function

(1)The determination of α -t curve

To determine the corrosion reaction mechanism function, it need to translate the relation curve between corrosion gain and time into thermal analysis curve in the constant temperature. Due to the limitation of experiment conditions, the test cannot be indefinitely to the end of the corrosion, it only proceed 20 hours. Therefore, it must assume that the corrosion reaction to the end of the 20 hours to calculate α [10]. So it can be defined as:

$$\alpha = \frac{w - w_0}{w_{20} - w_0} = \frac{\Delta w}{\Delta w_{20}} \eta_d = \frac{W_1}{E_d} \quad (9)$$

In the formula: w is the quality of the specimen in time t ; w_0 is the initial specimen quality; w_{20} is the quality of the test at the end of the experiment.

(2)Linear fitting of $G(\alpha)$ -t curve and error analysis of fitting

According to corrosion of alpha t curve to determine the most probable mechanism functions of corrosion reaction process and types of corrosion process. First, according to the experiment data it initiate the linear fitting with different reaction mechanism model function ;Second, according to the result of fitting it makes the error analysis to choose the best corrosion reaction mechanism function. The common reaction kinetics model functions that fitting calculation used are shown in Table 1.

Table1. Reaction kinetic model functions

number	function modes	symbol	$f(\alpha)$	$G(\alpha)$
1	Avrami-Erofeev equation (the secondary nucleation and growth interface reaction)	A2	$2(1 - \alpha)[- \ln(1 - \alpha)]^{\frac{1}{2}}$	$[- \ln(1 - \alpha)]^{\frac{1}{2}}$
2	Shrinkage of cylinder (area) phase boundary reaction (2d)	R2	$2(1 - \alpha)^{\frac{1}{2}}$	$1 - (1 - \alpha)^{\frac{1}{2}}$
3	Contraction ball (volume) phase boundary reaction (3 d)	R3	$3(1 - \alpha)^{\frac{2}{3}}$	$1 - (1 - \alpha)^{\frac{1}{3}}$

4	Parabolic rule (one dimensional diffusion)	D1	$\frac{1}{2}\alpha^{-1}$	α^2
5	Valensi equation (two- dimensional diffusion)	D2	$[-\ln(1-\alpha)]^{-1}$	$\alpha + (1-\alpha)\ln(1-\alpha)$
6	Jander equation (three- dimensional diffusion)	D3	$\frac{3}{2}(1-\alpha)^{\frac{2}{3}}\left[1-(1-\alpha)^{\frac{1}{3}}\right]^{-1}$	$\left[\frac{1-(1-\alpha)^{\frac{1}{3}}}{1-(1-\alpha)^{\frac{1}{3}}}\right]^2$
7	Ginstring- Brounshtein equation (three- dimensional diffusion)	D4	$\frac{3}{2}\left[(1-\alpha)^{-\frac{1}{3}}-1\right]^{-1}$	$1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}$

The specimen B, C, D, $G(\alpha)$ -t curve linear fitting results are similar to specimen A, so they are omitted here.

Base on $G(\alpha)$ -t curve linear fitting results of all sorts of function model in Table 1, it makes linear error analysis, and according to the result of the error, it selects the reaction mechanism function. Error calculation put α in different test conditions into the common reaction kinetics model of function in table 1, to calculate the relative error SD of $G(\alpha)$ -t fitting curve between calculated value and measured value [11, 12]. It defines the SD for:

$$SD = \sqrt{\frac{\sum_{i=1}^n |G(\alpha)_{ce} - G(\alpha)_{ni}|^2}{n}} \quad \eta_d = \frac{W_1}{E_d} \quad (10)$$

In the formula: $G(\alpha)_{ce}$ is calculated value of measuring; $G(\alpha)_{ni}$ is the calculated value of fitting.

Some reaction model functions $G(\alpha)$ are meaningless when $\alpha = 1$, it need to remove $\alpha = 1$ and calculate again. The value of n is related to calculate points.

After calculation for four specimens SD values are showed in Figure 1 a) ~ b).

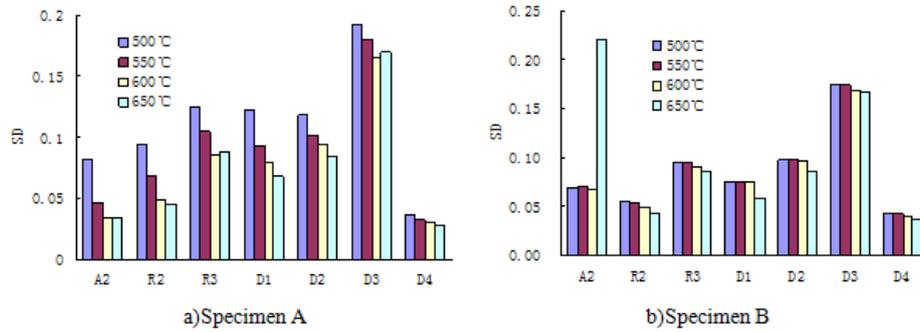


Fig.1. SD of reaction kinetic model functions for four specimens

It can be seen from the error analysis result of kinetics reaction mode function in different reaction temperature.

(3) The choice of reaction mechanism function

According to the SD histogram analysis of different reaction kinetics model function of specimen, it shows that the error analysis results of reaction function model D4 is minimum to every specimen, so it determine the reaction function model D4 is the reaction mechanism function. That is, the reaction mechanism follows three dimensional diffusion reaction types.

The mechanism function is:

$$G(\alpha) = 1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} \eta_d = \frac{W_1}{E_d} \quad (11)$$

$$f(\alpha) = \frac{3}{2} \left[(1 - \alpha)^{\frac{1}{3}} - 1 \right]^{-1} \quad (12)$$

5 Determination of kinetic triplet

After determining of dynamics model function, the integral form reaction kinetics equation and differential form is known. It shows in formula (11) and (12). On the derivative calculation, the constant k by the experience formula that Arrhenius put forward can be obtained, The k is closely related to the temperature.

After the mathematical transformation of Arrhenius empirical formula, it obtains the formula:

$$\ln k = \ln A - E / RT \quad (13)$$

Putting the value of k in different reaction temperature into above formula, it can obtain a set of $\ln k$ and T , and linear fitting of the $\ln k - 1 / T$, fitting results are shown in figure 2 (a) ~ (b).

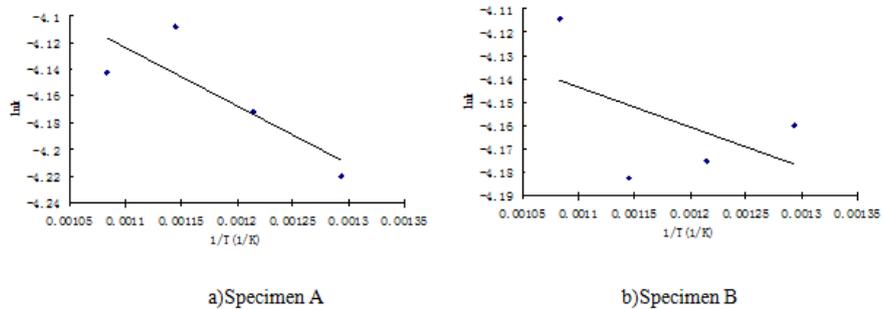


Fig. 2. Lnk-1/T linear fitting for the four specimens

According to the linear fitting and mathematical calculation, it can obtain:
Expression of specimen A is:

$$\ln k = -437.17 \frac{1}{T} - 3.6427 \quad (14)$$

Expression of specimen B is:

$$\ln k = -171.11 \frac{1}{T} - 3.9553 \quad (15)$$

Expression of specimen C is:

$$\ln k = -76.45 \frac{1}{T} - 4.0375 \quad (16)$$

Expression of specimen D is:

$$\ln k = -123.67 \frac{1}{T} - 4.0131 \quad (17)$$

As R is plots constant, R=8.31, it obtained E and A value by calculation.
After calculation, it obtain the kinetic triplet.

6 Analysis of corrosion kinetics equation

According to the dynamic reaction model equation and the kinetic triplet, the corrosion kinetics equation can be obtained.

Plugging the data into table 3 in the dynamic reaction model equation:

Corrosion kinetics equation of specimen A is:

$$\frac{d\alpha}{dt} = 0.039272 \exp\left(-437.17 \frac{1}{T}\right) \cdot \left[(1-\alpha)^{-\frac{1}{3}} - 1\right]^{-1} \quad (18)$$

Corrosion kinetics equation of specimen B is:

$$\frac{d\alpha}{dt} = 0.028729 \exp\left(-171.11 \frac{1}{T}\right) \cdot \left[(1-\alpha)^{-\frac{1}{3}} - 1\right]^{-1} \quad (19)$$

Corrosion kinetics equation of specimen C is:

$$\frac{d\alpha}{dt} = 0.026462 \exp\left(-76.45 \frac{1}{T}\right) \cdot \left[(1-\alpha)^{-\frac{1}{3}} - 1\right]^{-1} \quad (20)$$

Corrosion kinetics equation of specimen D is:

$$\frac{d\alpha}{dt} = 0.027116 \exp\left(-123.67 \frac{1}{T}\right) \cdot \left[(1-\alpha)^{-\frac{1}{3}} - 1\right]^{-1} \quad (21)$$

According to parameter values of the kinetic triplet and the dynamic equation, the four specimens follow the D4 reaction mechanism in the simulated corrosion environment, and based on the reaction activation energy E , the reaction activation energy of specimen A is the largest, it followed by specimen B, D, the specimen C is minimum. It obtains that the corrosion resistance of four specimens in the corrosion test is $A > B > D > C$ from the reaction activation energy values, it is consistent with the macro morphology observation of test surface and corrosion weight value analysis results.

7 Conclusion

(1) According to the Mass gain curves in different reaction temperature can be divided into two stages: the first stage, the corrosion weight gain basic approximate straight rose; The second stage, slow corrosion weight, it was similar to a parabola shape. It shows that four specimens have a certain ability to resist corrosion.

(2) Based on the theory of thermal analysis kinetics analysis, it established heterogeneous reaction dynamic equation model in the condition of constant temperature as a model of the corrosion process. Corrosion weight curve is obtained by thermal analysis of α -t curve, according to $G(\alpha)$ -t linear fitting curve and the fitting error analysis it determines the corrosion reaction type is reaction function mode D4. After calculation it can be known that the four specimens corrosion kinetics equation of the simulated corrosion environment conforms with reaction equation D4. Thereinto, corrosion reaction activation energy E of specimen A is 3632.88 J/mol, pre-exponential factor A is 0.026181558 s⁻¹; corrosion reaction activation energy E of specimen B is 1421.92 J/mol, pre-exponential factor A is 0.019152922 s⁻¹; corrosion reaction activation energy E of specimen C is 635.30 J/mol, pre-exponential

factor A is 0.017641521 s⁻¹; corrosion reaction activation energy E of specimen D is 1027.70 J/mol, pre-exponential factor A is 0.018077269 s⁻¹.

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