

# Kinetic Analysis of High Temperature Corrosion on Straw Boiler Heating Surface

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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*

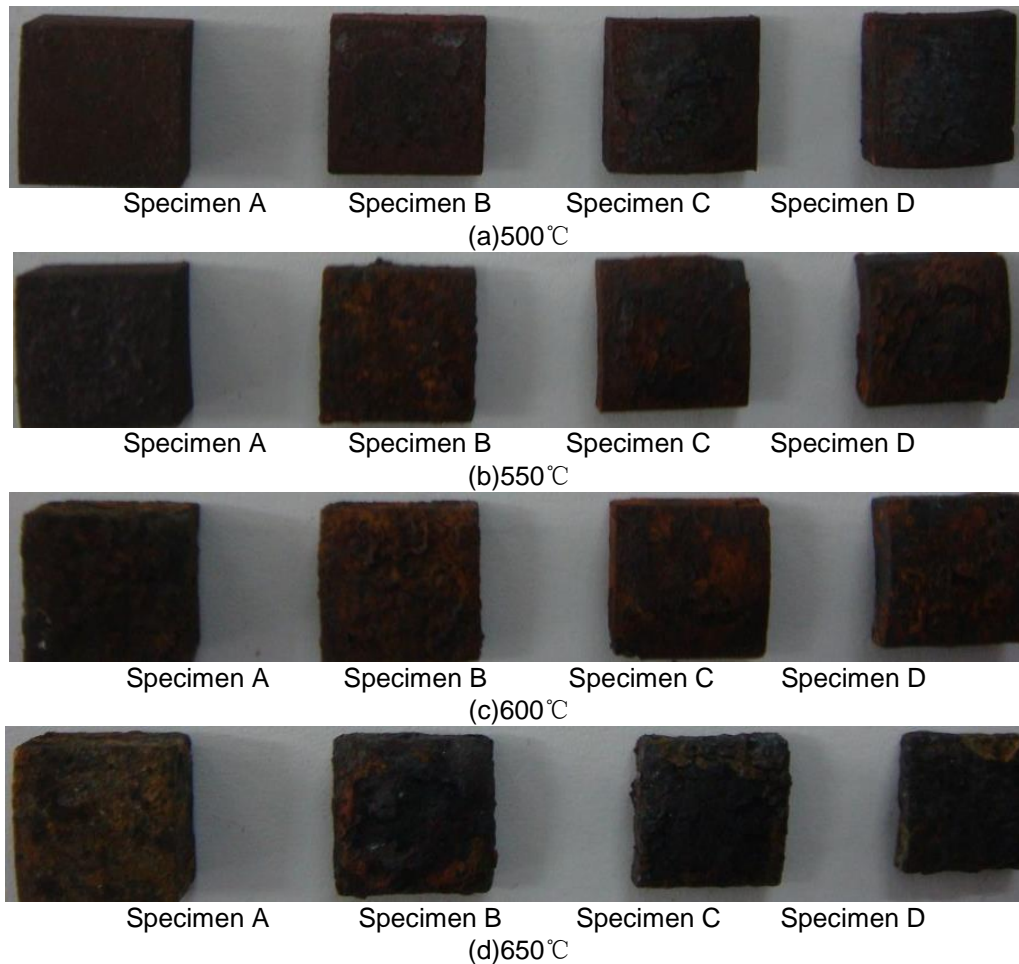
## 1. Introduction

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. Heating Surface Corrosion Simulation Test

In the corrosion simulation test, 20G[1], 12Cr1MoVG[1-3], 1Cr19Ni11Nb(TP347H)[1-2,4-8] and 10Cr9Mo1VNb(T91)[1-2,7] are made into the specimen A,B,C,D respectively, it smear the corrodent of quality ratio that  $KCl:NaCl:K_2SO_4:Na_2SO_4=63:13:5:1$  on the specimen surface. The cycle corrosion experiment with reaction temperature of 500°C, 550°C, 600°C and 650°C, removing the specimen and weighting every 2 hours, total time is 20 hours.

After the simulated corrosion test, the reaction temperature corrosion specimen photos as shown in Figure 1 (a), (b), (c) and (d). It can be found from the photos the specimen surface corrosion is serious with the increasing of reaction temperature, the corrosion layer is more thick. At 500 °C and 550 °C, the process of corrosion of four specimens is slow. At 600 °C and 650 °C, the corrosion is obviously quickened, the corrosion is serious especially at 650 °C. From the Figure 1 it can be seen that the corrosion resistance of specimen A is best, then the specimen B, specimen C and D is the worst. At 500 °C and 550 °C, four types of specimen has certain corrosion resistance; At 600 °C, the specimen A and B still has certain corrosion resistance, the corrosion resistance of specimen C, D is obviously decreased; At 650 °C, only the specimen A have the certain ability to resist corrosion, the specimen B, C, D basically lost the corrosion resistance, the specimen C, D have totally lost the corrosion resistance.



**Figure 1. Macro-morphologies of Each Corrosion Specimen Surface at Four Temperatures**

Figure 2 a), b), c) and d) respectively are the corrosion weight curve of four specimens in different reaction temperature within the range of 500 ~ 650 °C, that is the change in the relationship between corrosion weight and time. In Figure 2, it shows that four specimens in different reaction temperature corrosion can be divided into two stages: the first stage, the corrosion weight is quickly, basic approximate straight rise; The second stage, the corrosion commence slowing down, the speed of dynamiting drop, it similar to a parabola. This illustrates the four kinds of pipes has certain corrosion resistance.

In Figure 2, it can be found the corrosion rate of weight gain of four pipe are greatly increased with the reaction temperature rising, especially at 650 °C, its performance is more obvious.

In Figure 2 a), as the temperature of specimen A below 600 °C, the corrosion rate of weight gain is low, as the temperature rise to 650 °C, the corrosion rate of weight gain increase rapidly, the experimental data shows this corrosion rate of weight gain is more than twice the corrosion rate of weight gain at 600 °C.

In Figure 2 c) and d), it can be seen that the corrosion rate of weight gain of the specimen C and D in the temperature below 550 °C is low, when the temperature rises to more than 600 °C, the corrosion rate of weight gain increases rapidly, especially at 650 °C, mass gain curve into a straight line. it shows that , the specimen C and D almost lost the corrosion resistance when the reaction temperature above 600 °C.

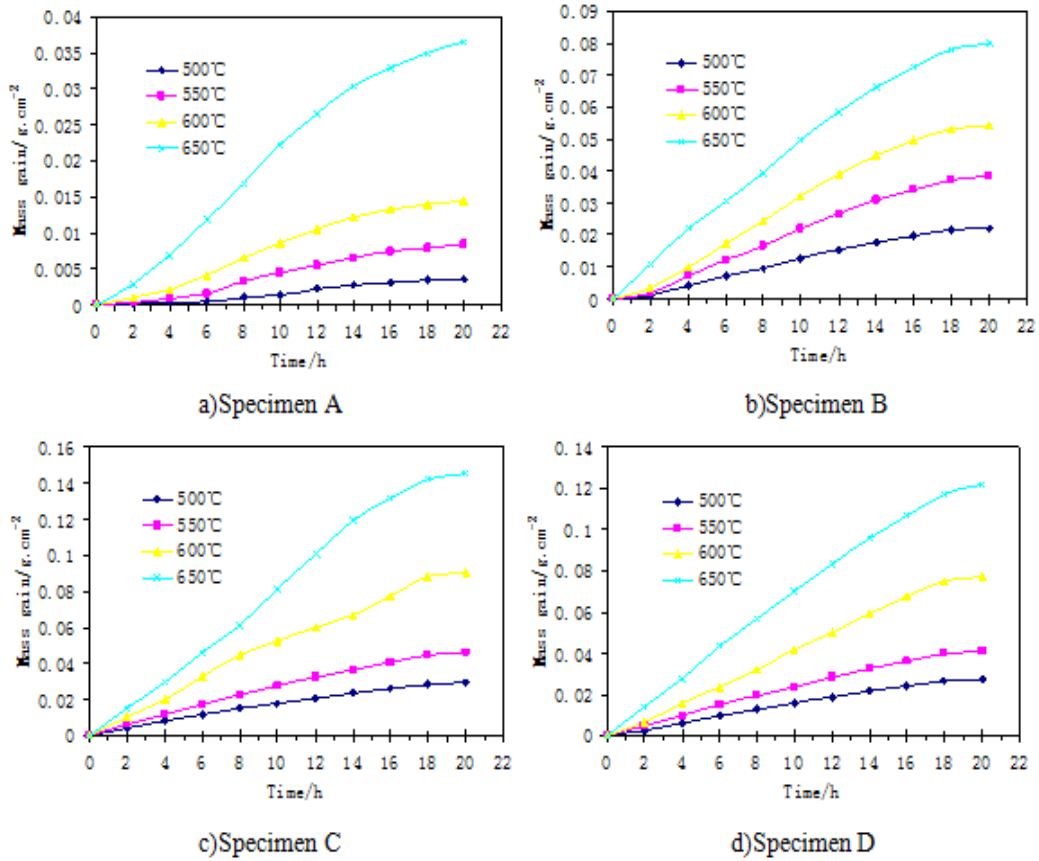


Figure 2. Mass Gain Curves of Four Specimens at Different Temperatures

### 3. 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:  $\alpha$  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:

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

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

Due to the above equation are listed in isothermal condition, the formula (7) and (8) are also known as heterogeneous reaction dynamics equation in the condition of constant temperature.  $E$ ,  $A$  and  $f(\alpha)$  is called the kinetic triplet.

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  $\Delta W$  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

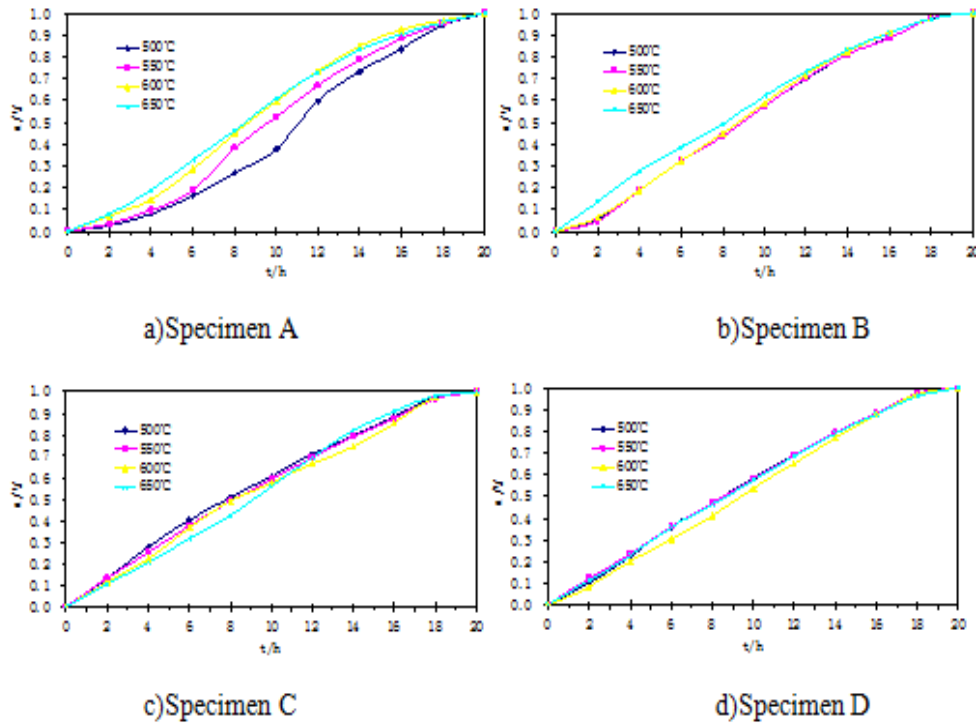
(1)The determination of  $\alpha$  -t curve

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  $\alpha$  [10]. So it can be defined as:

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

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.

The thermal analysis  $\alpha$  -t curves of different specimens are obtained in different reaction temperature are shown in Figure 3.



**Figure 3. The  $\alpha$  -T Curves of Four Specimens at Different Temperatures**

(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.

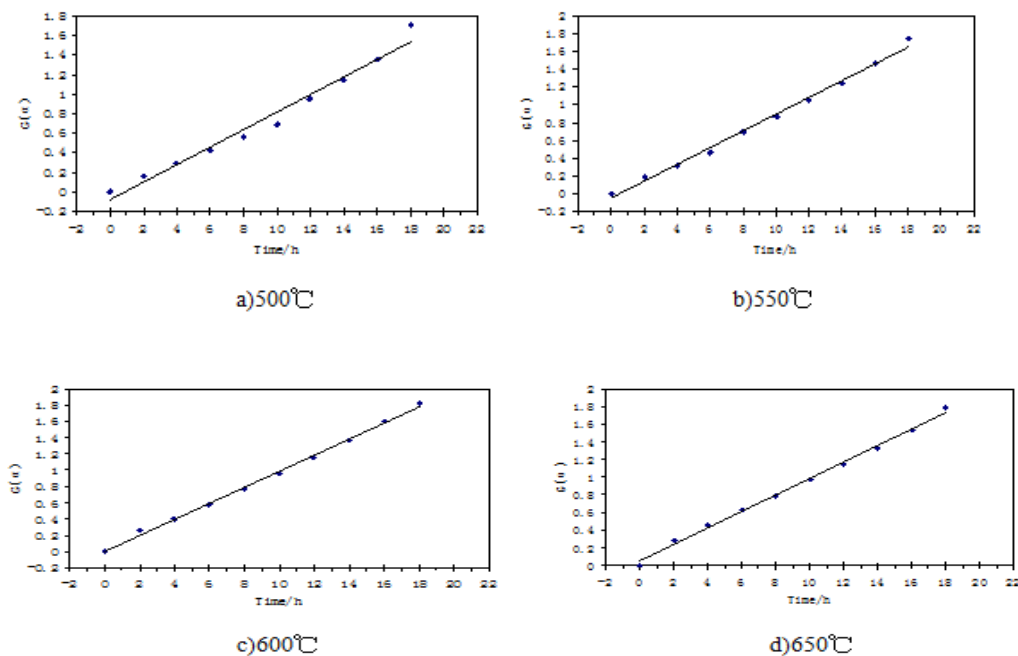
**Table 1. Reaction Kinetic Model Functions**

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 (3d)	R3	$3(1-\alpha)^{\frac{2}{3}}$	$1-(1-\alpha)^{\frac{1}{3}}$
4	Parabolic rule (one dimensional diffusion)	D1	$\frac{1}{2}\alpha^{-1}$	$\alpha^2$

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

It focus on A2 to show the fitting result here, Figure 4 a) ~ d) show the  $G(\alpha)$ -t curve fitting results of reaction kinetics model function of specimen A in the reaction temperature.

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



**Figure 4.  $G(\alpha)$ -t Curves Linear Fitting for A2 at Different Temperatures**

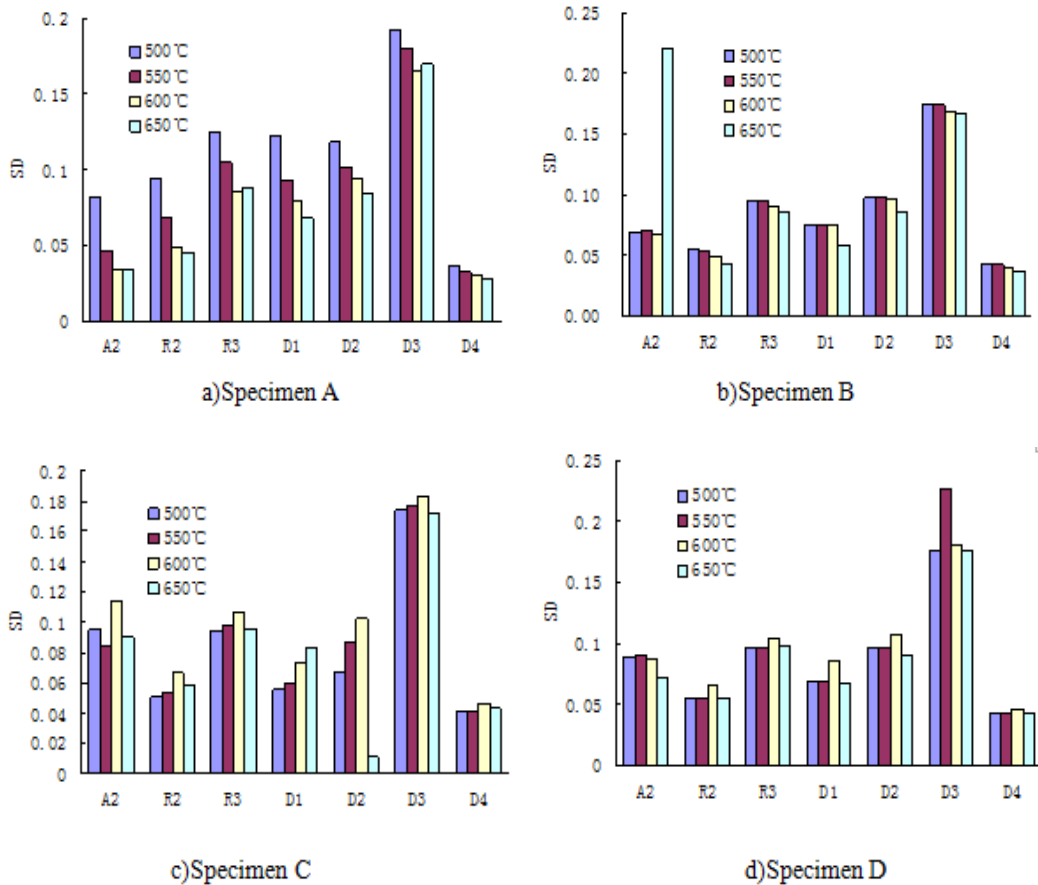
Base on  $G(\alpha)$ -t curve linear fitting results of all sorts of function model in Table 1, it makes linear error analysis, and according to the result of the error, it selects the reaction mechanism function. Error calculation put  $\alpha$  in different test conditions into the common reaction 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 define the SD for:

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

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 5 a) ~ d).



**Figure 5. 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:

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

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

## 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. The calculation results are shown in Table 2.

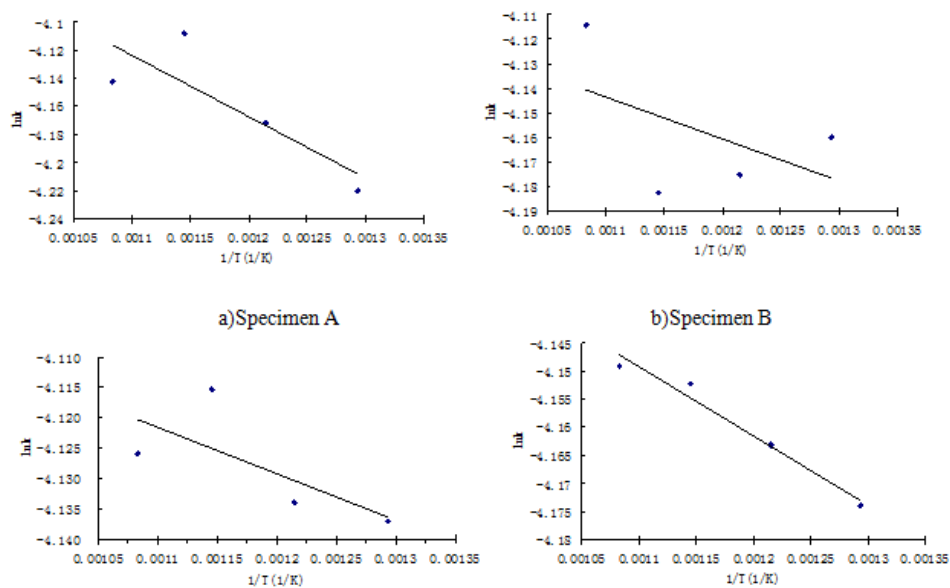
**Table 2. K of the Each Specimen at the Same Temperature**

Temperature/K	773	823	873	923
K-Specimen A	0.01470	0.01542	0.01644	0.01589
K-Specimen B	0.01561	0.01537	0.01526	0.01634
K-Specimen C	0.01597	0.01602	0.01632	0.01615
K-Specimen D	0.01539	0.01556	0.01573	0.01578

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 6 (a) ~ (d).



**Figure 6.  $\ln k - 1/T$  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, they are shown in Table 3.

**Table 3. E and A of the Each Specimen**

Materials	E/J·mol <sup>-1</sup>	A/s <sup>-1</sup>
Specimen A	3632.88	0.026181558
Specimen B	1421.92	0.019152922
Specimen C	635.30	0.017641521
Specimen D	1027.70	0.018077269

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 base 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 obtain 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 show that four specimens have a certain ability to resist corrosion.

(2) Base 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  $\alpha$ -t curve, according to  $G(\alpha)$ -t linear fitting curve and the fitting error analysis it determine 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  $0.026181558 \text{ s}^{-1}$ ; corrosion reaction activation energy E of specimen B is 1421.92 J/mol, pre-exponential factor A is  $0.019152922 \text{ s}^{-1}$ ; corrosion reaction activation energy E of specimen C is 635.30 J/mol, pre-exponential factor A is  $0.017641521 \text{ s}^{-1}$ ; corrosion reaction activation energy E of specimen D is 1027.70 J/mol, pre-exponential factor A is  $0.018077269 \text{ s}^{-1}$ .

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## References

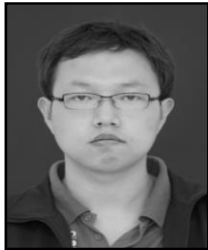
- [1] Z. Li, High temperature corrosion research of super heater in biomass boiler: (Master's Thesis). Beijing: North China Electric Power University, (2009).
- [2] H. P. Nielsen, F. J. Frandsen and K. Dam-Johansen, The implications of chlorine-associated corrosion on the operation of biomass-fired boilers. *Progress in Energy and Combustion Science*, vol.26, no.3, (2000), pp.283-298.
- [3] J. M. Yin and Z. S. Wu. Corrosion Characteristic of 12Cr1MoVG Subjected to Atmosphere of Superheaters in Biomass Boilers. *Power System Engineering*, vol.24, no.6, (2008), pp.41-44.
- [4] J. M. Yin and Z. S. Wu, Corrosive characters of TP347H steel in super heater's atmosphere of biomass-burned boiler. *Thermal Power Generation*, vol.38, no.7, (2009), pp.27-31.
- [5] S. Q. Zhao and X. S. Xie, Heats tissue temperature and improves research of super critical boiler super heater pipe. *Material Review*, vol.18, no.8, (2004), pp.131-133.
- [6] Q. Li, J. Z. Song and Z. G. Nie, Corrosion cause analysis of 130 t/h burning biomass boiler super heater pipe. *Power Generation Equipment*, vol.13, no.3, (2009), pp.214-218.
- [7] Z. G. Li, High-temperature oxidation research -material of Coal-fired power plants in super critical convection heating surface tubes, Annual Meeting of Chinese Chemistry Academic, (2009); Wuhan.
- [8] H. W. Song and H. W. Zhen, The researches on the mechanism of the biomass boiler high temperature super heater corrosion. *Boiler Manufacture*, no.5, (2010), pp.14-18.
- [9] R. S. Hu and Q. Z. Shi, Thermal analysis kinetics. Beijing: Science Press, (2001).
- [10] C. Y. Pan, High temperature corrosion research: (HCl) of super heater zones within the garbage incinerator. Hangzhou: Zhejiang University Press, (2004).
- [11] J. M. Yin, Y. H. Ding and Z. S. Wu, Dynamics study on corrosion test in gas-phase HCl for supper heaters of biomass boilers, *Thermal Power Generation*, vol.38, no.1, (2009), pp.10-13.
- [12] H. Zhao, Q. Zhang and G. J. Wu, A study of thermal analysis kinetics for high temperature corrosion of water wall tube. *Power System Engineering*, vol.25, no.6, (2005), pp.32-34.
- [13] Z. Y. Luo, C. Chen and C. J. Yu, Review of deposition and high-temperature corrosion in biomass-fired boilers. *Journal of Combustion Science and Technology*, vol.20, no.3, (2014), pp.189-198.

- [14] Z. F. Tian, S. X. Wang and Y. W. Cao, Analysis of mechanism and factors influencing the combustion of biomass fuels. *Journal of Anhui Agricultural Science*, vol.42, no.2, (2014), pp.541-543.
- [15] C. M. Geng, J. H. Chen, X. H. Wang, W. Yang, B. H. Yin, H. J. Liu and Z. P. Bai, Comparative study on the particle emission characteristics of biomass boiler with coal-fired industrial boiler. *Research of Environmental Science*, vol.26, no.6, (2013), pp.666-671.

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