Thermochimica Acta, 93 (1985) 281-285
Elsevier Science Publishers B.V., Amsterdam

ELECTROTHERMOGRAPHY AND ITS APPLICATION TO STUDY THE KINETICS OF HIGH-TEMPERATURE METAL-GAS INTERACTION

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ABSTRACT

The method for calculating kinetic parameters of the reaction of the **high** temperature interaction of metals with gases on the basis of the programmed heating of the metals thin threads or bands by electric current at their contact with reagent is described.

INTRODUCTION

To study the kinetic of high temperature interaction of metals with gases at 1000 - 3000 °C and the process times of "second" duration the set of methods and devices entitled as "electrothermographical method" /ETM/ was developed in the 70ths by the authors and co-workers. The method was based on the programmed heating of metals thin threads or bands by the electric current at their contact with the corresponding reagent. Experimentally the thermal non-gradient regime for the sample heating and the controlled hydrodynamic medium was attained. Three regimes of the sample heating were given by the outer operating arrangements :
1/ temperature stabilisation in the reaction.2/linear temperature variation /with the varying rate/. 3/ stabilised heating /on the sample/ by the electric current. The metal-gas interaction in the frames of the ETM was followed by the rate of chemical heat release /continious measurements/ by the thickness of the films of the condensed reaction products and the reacted metal /periodical metalographical and continuous conductometric measurements/. The initial information in the experiment is the sample temperature and also the drop of voltage on it and the strength of the current in the reaction process. The control for the thread temperature is achieved optically. The schemes of electronic observing devices are shown in [1] - [3]. The main technical characteristics of the systems are as follows :

Proceedings of ICTA 85, Bratislava

1/ The time of fixing the constant temperature of the thread from moment of the current feeding - /2 - 5/ 10^{-2} sec.

2/ The scanning rate by temperature -1 10^{2} - 5 10^{4} grad/sec.

3/ The time constant of power stabilisator - 10^{-5} sec.

4/ The threshold sensitivity by the rate of reaction heat-release -5 10^{-2} v.

The methods of calculating the kinetic constant using ETM derives from the analyses of nonstationary equation of heat balance at the chemical heat sources

$$c_p \varrho \frac{d}{4} \frac{dT}{dt} = \dot{q} /t/ + W /t/ - q_T /T/ \qquad (1)$$

where

c_p, ϱ are heat capacity and density of metal, d is the diameter of the thread, T is temperature, t is time, $\dot{q}$ is the rate of chemical heat release, W is electric power, q_T is resulting heat transfer.

While isothermic regime of heating up of the thread there is the compensation by a joule heating up of the change in chemical heat release intensity $\dot{q}$ and to determine $\dot{q}$ from 1 we have

$$\dot{q} /t/ = q_T - W /t/ \qquad (2)$$

The amount of the released heat q is found out by integrating (2) at the know value q_T. The last one is calculated either on the base of independent data or for the reactions with auto-retardation directly in the kinetic experiment after stopping the intense chemical heat-release $/q_T = \lim_{t \to \infty} W(t)/$.

Using the series of kinetic curves $\dot{q}$ /q/ the form of approximating kinetic function and constant values are chosen.

The procedure of determining the kinetic parameters in the frames of compensating variant of ETM may be simplified. If the class of the kinetic function is know in advance. Thus at the degree laws of interaction of the type $\dot{q} = K/q^{n}$ /n = 1,2 parabollic, cubic equations/ which are often realized at the metal-gas interaction using integral of the kinetic equation and the equation (2) we obtain

$$W /t/ = q_T - \frac{K^{1/(n+1)}}{\left[(n+1)t\right]^{n/(n+1)}} \qquad (3)$$

Since accounting that q_T = const to determine the form of the kinetic function /the value of parameter n/ and the constant it is sufficient to obtain the straghting of the values W by varying the $t^{-n/n+1}$ values. In the given case for determining the kinetic constants there is no need to know absolute values $\dot{q}$/t/ and q_T.

That method of calculating the kinetic parameters is widely used in the experimental investigations.

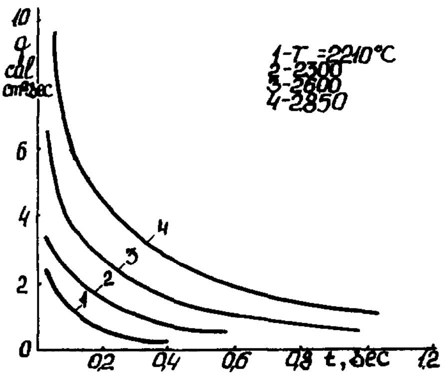

Fig. 1. Shows the curves obtained on the base $\dot{q}$/t/ at tantalum nitriding corresponding the kinetic equation of parabollic type

$$\dot{q} = \frac{2,1.10^5 \exp(-\ 62000/RT)}{q}, \quad \frac{cal}{cm^2\ .\ sec}$$

Under non-isothermic conditions may exist scanning and spontaneous regimes of the thread heating up. In the first case the change law of thread temperature is given by outer apparatus independent on the intensity of chemical heat release /compensating heating up by joule power/. Then at autoretardation reaction the methodology of finding the value $\dot{q}$ is restricted by the registration the electric power W at the reaction /initial/ and idle /repeated/ threads heatings up

$$\dot{q} = W'/t/ - W''/t/ \qquad (4)$$

It should be noted that there is no need to calculate the derivative dT/dt.

In the second case the thread heating up is achieved by the stabilised electrical power /W=const/. According to this the character of temperature change in the sample is followed by the dynamics of heat release and heat transfer. Two process regimes are possible here devided by the critical condition /$W = W_*$/. At $W < W_*$ the reaction proceedss rather slow and the maximum thread temperature slightly exceeds the stationary value. At $W > W_*$

sample heating up results in the heat self-ignition. Below the limit of ignition /$W < W_*$/ the value $\dot{q}$ may be determined directly from 1 if other components are known. It should be reasonable to calculate the results by ECM. Under the limit of ignition /$W \geq W_*$/ the rate of heat release may be obtained in the frames of solving the reverse problem of ignition theory [4] . The dependence of ignition limit as well as the induction period are determined experimentally from parameter process and then using known schemes [5] and [6] the constants of reaction at the ignition are calculated.

It is more difficult to get the kinetic data by non-isothermic methods than by isothermic ones though they appear to be very fruitful while study the complex multi-stage reactions because there is a possibility to carry out their partial division due to the different temperature dependences of constants at separate stages.

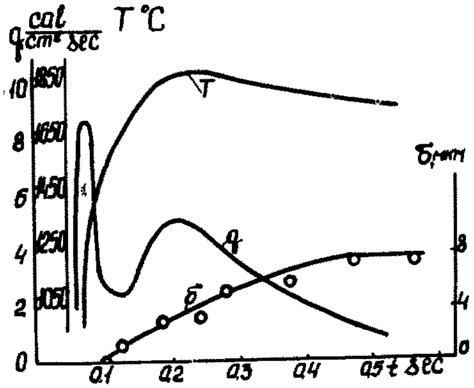

Fig. 2. Shows the rate of change of heat-release $\dot{q}$ and the layers thickness of products δ under the non-isothermal conditions at the heating up of zirconium thread in the nitrogen by the stabilised electric power. The first maximum of $\dot{q}$ value is connected with the soluting in nitrogen metal, the second is connected with the appearance and growth of nitride phases.

In the conclusion it should be noted that the described method of ETM presents the development of calorimetric and thermographic approaches in applying to the metal-gas interaction. But due to the fact that in ETM the sample is simultaneously the reagent, the source of high temperature and temperature sensor, one can avoid the principal difficulties inherent to classical schemes and carry out the measurements in parameters non-available earlier for the experimental investigations.

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