Process Design for the Shape Controlling of Pulled Growth Crystal

*Lunyong Zhang**1, Hongbo Zuo2, Jianfei Sun*1, Dawei Xing1, Jiecai Han2, Xiaohong Wang2*

1. School of Materials Science and Engineering, Harbin Institute of Technology, Harbin, PRChina, 150001

2. Center for Composite Materials, Harbin Institute of Technology, Harbin, PRChina, 150001

Corresponding Author：*Jianfei Sun* jfsun_hit@263.net
Lunyong Zhang *allen.zhang.ly@gmail.com*

Abstract：A model relating the diameter variation with the process parameters during a practical crystal growth by pulling has been proposed. The crystal shape evolution under various growth process was analysed. The results prove, in theory, that the most effective and convenient measure to control the crystal diameter is adjusting the pulling rate, and the optimal process for growing a equal diameter crystal is simultaneously decreasing the pulling rate and the heater temperature with dropped decreasing rate. Moreover, the model could be used for designing the process for growing a crystal with a desired shape.

Keyword：crystal growth, shape design, process design, numerical method

1. Introduction

It is well known that the diameter of a crystal grown by techniques with pulling process such as the Czochralski method[1] and the Kyropoulos method[2] needs to be controlled carefully since two reasons: maximizing productivity of the desired size crystal and ensuring the stability of growth condition so that reducing defects. This task was achieved to date generally by optical control or weight control, depending on the crystal material[3].These technical measures, in fact, just play a role of monitoring the crystal diameter whose adjustment so control is fully realized by adjusting the growth conditions. Therefore, a response function, *i.e.* the relation between the diameter or the diameter variation and the growth conditions, is quite important.

In the past research, several simple relations concerning the factors influencing crystal diameter have been proposed for different growth stages of the Czochralski method through simplified energy conservation analysis based on geometrical approximation. Several concepts for example the diameter inertia have been introduced[4]. They indicated that crystal diameter can positively feedback to itself's increase during the shoulder-expanding process and would bear a higher increase rate at a larger shoulder-expanding angle when the shoulder-expanding angle is fixed, and decreasing melt temperature, crystal diameter and rotation rate or enhancing heat exchange ability can improve the stability of the crystal diameter encountered a melt temperature variation[4]. G. Singh *et.al* stated that the growth front shape but not its curvature is a dominant factor affecting the crystal shape of the Kyropoulos method[5]. These relations are benefit for understanding the crystal shape evolution, however, their lacking of relating the crystal diameter or its variation to the growth conditions including the melt temperature, the pulling rate and the rotation rate[6] has obstructed their application in the quantitatively controlling of crystal diameter.

A geometric model describing the diameter variation of a crystal grown by pulling has been suggested in a previous paper of us[7]. Its analysis showed the variation trend, *i.e.* increasing or decreasing of the diameter, and the corresponding variation rate are determined intrinsically by the pulling rate, the slope of the fringe of the growth front as well as the advance speed of the front fringe in the crystal radial direction. The interesting is that the crystal diameter is self-stabilized when the factors mentioned here is fixed during the growth, which shows us a promise of growing perfect equal-diameter crystal. Unfortunately, keeping the factors constant is quite difficult at present because the latter two factors are controlled by the pulling rate and the heat field in practice. That implies it is necessary to introduce a relation among the latter two factors, the pulling rate and the heat filed into the geometric model for its application in the analysis of a specific crystal growth system.

In principle, the pulled growth of a pure crystal could be approximately considered as a directional solidification process for which the solidification rate namely the advance rate of the solid-liquid interface has been quantitatively related to boundary temperatures which solely controls the process for a give directional solidification system[8]. Therefore, this paper aims to apply the geometric model we have proposed to a pracitcal crystal growth system with pulling and without the growth front shape varying much during the growth, *e.g.* the Kyropoulos method and the SAPMAC method[9], through integrating the solidification rate relation of a directional solidification process. Further, the effects of growth parameters on the crystal shape evolution will be discussed at length and finally, the feasibility of utilizing the model to design crystal shape is displayed.

2. Model

According to Ref [7], shape evolution of a crystal grown by pulling can be described by the derivative of the crystal shape function $h=S(r)$, where r and h are the radius and the height of the crystal, respectively. The derivative of the crystal shape function bears a relation as follow

$$\dot{S}(r)=\frac{\left[\frac{u}{v_{//}}+\left(1-\frac{\rho_{\mathrm{c}}}{\rho_{\mathrm{m}}}\right)\frac{r^2}{R^2}\dot{f}\right]\dot{f}}{\frac{u}{v_{//}}+\left(1-\frac{r^2\rho_{\mathrm{c}}}{R^2\rho_{\mathrm{m}}}\right)\dot{f}} \tag{1}$$

where u is the pulling rate, $v_{//}$ is the radial advancing speed of the fringe of the growth front, R is the radius of crucible. $\dot{f}$ is the slop of the growth front at its fringe, $f(r)$ represents the shape function of the growth front. ρ_m and ρ_c are melt density and crystal density, respectively. Moreover, the variation rate of the crystal height can be written as[7]

$$\frac{dh}{dt}=\left[\frac{R^2}{R^2-r^2}u+\frac{r^2}{R^2-r^2}\left(1-\frac{\rho_{\mathrm{c}}}{\rho_{\mathrm{m}}}\right)\dot{f}\,v_{//}\right] \tag{2}$$

and the variation rate of the crystal radius could be written as follow

$$\frac{dr}{dt}=\frac{dr}{dh}\cdot\frac{dh}{dt}=\left(\dot{S}\right)^{-1}\frac{dh}{dt} \tag{3}$$

Therefore, the crystal height and the crystal radius could be obtained as

$$h=\int_0^t\left[\frac{R^2}{R^2-r^2}u+\frac{r^2}{R^2-r^2}\left(1-\frac{\rho_{\mathrm{c}}}{\rho_{\mathrm{m}}}\right)\dot{f}\,v_{//}\right]dt \tag{4}$$

and

$$r=r_0+\int_0^t\left[\frac{R^2}{R^2-r^2}u+\frac{r^2}{R^2-r^2}\left(1-\frac{\rho_{\mathrm{c}}}{\rho_{\mathrm{m}}}\right)\dot{f}\,v_{//}\right]\frac{\frac{u}{v_{//}}+\left(1-\frac{r^2\rho_{\mathrm{c}}}{R^2\rho_{\mathrm{m}}}\right)\dot{f}}{\left[\frac{u}{v_{//}}+\left(1-\frac{\rho_{\mathrm{c}}}{\rho_{\mathrm{m}}}\right)\frac{r^2}{R^2}\dot{f}\right]\dot{f}}dt \tag{5}$$

r_0 is the radius of the seed.

To analysis the effects of growth parameters on the crystal shape evolution during a practical crystal growth and design the growth process for a desired shape crystal, relations between the growth parameters and $\dot{f}$ as well as $v_{//}$ must be introduced. For the Kyropoulos method and the SAPMAC method, the growth front is cone shaped and the cone angle is always little varied, about 90°, so that $\dot{f}$ could be regarded as a constant, about -1[10]. We adopted the equation relating the crystallization rate, v, with the heater temperature, T_{H}, during a 1-D crystallization process of pure material[8].

$$T_{\mathrm{H}} = T_{\mathrm{M}} - \left[\frac{D_l}{k_l} \Delta H + \frac{k_s D_l \left(T_{\mathrm{M}} - T_{\mathrm{C}} \right)}{k_l D_s \left(1 - e^{-v\alpha / D_s} \right)} \right] \left(1 - e^{-vL/D_l} \right) \tag{6}$$

When the crystallization rate is enough small, a condition is always satisfied for a practical crystal growth, this relation could be simplified as

$$T_{\mathrm{H}} = T_{\mathrm{M}} - \left[\frac{\Delta H v}{k_l} - \frac{k_s \left(T_{\mathrm{M}} - T_{\mathrm{C}} \right)}{k_l \alpha} \right] L \tag{7}$$

where T_{C} is the temperature of the cooler, T_{M} is the melt temperature of the crystallization material, ΔH is the latent heat, k_s and k_l are the thermal conductivity coefficient of the crystal and the melt, respectively. α is the distance from the crystallization interface to the cooler, $\alpha=h$ for the crystal growth process considered in this paper. L is the distance from the crystallization interface to the heater, it can be written as follow for a crystal growth with pulling according to Ref [7]

$$L = L_0 - \int_0^t \frac{r^2}{R^2 - r^2} \left[v_{//} \dot{f} \left(1 - \frac{\rho_{\mathrm{c}}}{\rho_{\mathrm{m}}} \right) + u \right] dt \tag{8}$$

L_0 represents the initial distance between the melt level and the heater.

Based on Eq.7, the crystallization rate is

$$v = \frac{1}{\Delta H} \left[\frac{k_l \left(T_{\mathrm{M}} \text{-} T_{\mathrm{H}} \right)}{L} + \frac{k_s \left(T_{\mathrm{M}} - T_{\mathrm{C}} \right)}{h} \right] \tag{9}$$

Since the growth front is inclined to the level for the Kyropoulos method and the SAPMAC method, the crystallization rate namely the speed at which the growth front advances in the crystal axial direction bears a geometric relation as shown in Fig.1 with the radial advancing speed of the growth front fringe . As a consequence, the radial advancing speed of the growth front fringe can be expressed as

$$v_{//}=-\frac{v}{\dot{f}}=-\frac{1}{\Delta H\,\dot{f}}\left[\frac{k_l\left(T_{\mathrm{M}}-T_{\mathrm{H}}\right)}{L}+\frac{k_s(T_{\mathrm{M}}-T_{\mathrm{C}})}{h}\right] \tag{10}$$

Obviously, the crystal shape can be depicted through calculating Eq.4, 5, 8 and 10 with numerical difference method, so the effects of the growth parameters on the crystal shape evolution also can be discussed. The physical quantities of sapphire crystal used for the following calculation are T_C=2200K, T_M=2323K[11], ΔH=4.38×10^9Jm^{-3}[11], k_s and k_l are 3.5Js^{-1}m^{-1}K^{-1}[12], ρ_s=3980 Kgm^{-3}[13], ρ_l=3175Kgm^{-3}[13], r_0=5mm, L_0=500mm, R=150mm.

3. Effects of process parameters on the crystal shape evolution

Ref [7] has been shown that decreasing the pulling rate, and increasing the slop and the radial advancing speed of the fringe of the growth front could, in most cases, depress the decrease rate or enhance the increase rate of the crystal diameter. This is a general view how the crystal shape could be influenced. For a practical growth process, the knowledge of the effects of growth process parameters on the crystal shape evolution is more applicable.

Fig.2 exhibits the crystal shapes calculated under fixed pulling rate (U1 route) and on-line decreased pulling rate (U2 route). It is shown that the crystal is cone shaped under constant pulling rate and heat temperature since the radial advancing speed of the fringe of the growth front rapidly decreases after the growth starting. Decreasing the pulling rate could obviously depress the decrease rate of the radial advancing speed of the fringe of the growth front (Fig.2b) besides directly reducing the decrease of the crystal diameter caused by the raise of the growth front[7], so that the decrease rate of the crystal diameter was reduced and the crystal diameter could even be increased by a enough large decrease of the pulling rate. Consequently, multi-times on-line decreasing the pulling rate could grow a crystal with proximately equal diameter.

Fig.3 shows the crystal shapes calculated under different process routes of heater temperature. We can see decreasing heater temperature could enhance the radial advancing speed of the fringe of the growth front so reduce the decrease rate of the crystal diameter after the shoulder-expanding, and even cause that the crystal diameter rapidly increases since $v_{//}$ gradually increases after a duration of growth. Fig.4 indicates, when the diameter starts to rapidly increase, the heater temperature has decreased to below the melt temperature of sapphire crystal. That implies the crystal grows in a undercooled melt, which is generally not desired during a practical crystal growth. Therefore, a crystal with proximately equal diameter can not be grown solely by on-line decreasing the heater temperature.

The analyses above seems to suggest keeping the heater temperature and on-line decreasing the pulling rate is the best process for growing equal diameter crystal. However, Fig.2b displays under a fixed heater temperature the radial advancing speed of the fringe of the growth front will be zero after the crystal growing to a certain height, that means the crystal would stop growth even the pulling rate is decreased to zero under a fixed heater temperature, so it is better to decrease the heater temperature on-line in company with on-line decreasing of the pulling rate, which is a commonly used process for a practical crystal growth. From Fig.5, we can see simultaneously on-line decreasing the pulling rate and the heater temperature remarkably, compared with the other two types of process, increased the height of crystal section with equal diameter. Two sapphire crystals experimentally grown under processes similar with the two process routes shown in the Fig.5 as examples of simultaneously on-line decreasing the pulling rate and the heater temperature are displayed in Fig.5e and f, it can be seen the crystal shapes are quite like the calculated shapes.

4. Process design for the crystal with a designed shape

Eq.1 and Eq.10 indicate the slop of a crystal shape is a function of the pulling rate and the heater temperature for a given pulled growth system when the slop of the fringe of the growth front does not noticeably change, which suggests that for a pre-determined $\dot{S}(u, T_{\mathrm{H}})$ a process parameter could be designed when another process parameter has been given. In other words, the crystal shape as well as the corresponding growth process could be designed. The process design formulae could be written as follow

$$u=-\frac{1}{\Delta H R^{2}}\left(\frac{\rho_{\mathrm{c}}}{\rho_{\mathrm{m}}} r^{2}+\frac{r^{2}\dot{f}-R^{2}\dot{S}}{\dot{S}-\dot{f}}\right)\left[\frac{k_{s}(T_{\mathrm{M}}-T_{\mathrm{C}})}{h}+\frac{k_{l}\left(T_{\mathrm{M}}-T_{\mathrm{H}}\right)}{L}\right] \tag{11}$$

$$T_{\mathrm{H}}=T_{\mathrm{M}}+\left[\Delta H R^{2}\left(\frac{\rho_{\mathrm{c}}}{\rho_{\mathrm{m}}} r^{2}+\frac{r^{2}\dot{f}-R^{2}\dot{S}}{\dot{S}-\dot{f}}\right)^{-1} u+\frac{k_{s}(T_{\mathrm{M}}-T_{\mathrm{C}})}{h}\right]\frac{L}{k_{l}} \tag{12}$$

Fig.6 gives out a sapphire crystal whose shape is designed with a linear slop function. Fig.7 and Fig.8 are two exemplified processes designed for growing the crystal shown in Fig.6. It is shown that the designed heater temperature would be extraordinary high at the early stage of the growth if the pulling rate is pre-given. Considering setting up a high heater temperature condition is much more difficult than setting up a high pulling rate condition during a practical crystal growth, we suggest firstly determining the heater temperature process and then calculating the pulling rate according to the designed slop function of the crystal shape.

5. Conclusion

This paper has applied the shape evolution model proposed in a paper recently published by us through integrating the quantity kinematical relation for a one dimensional crystallization process to analyse the effects of growth process parameters on the crystal shape during a practical growth by pulling and to design the shape of a crystal. It has been shown that the optimal process for growing a equal diameter crystal is simultaneously reducing the pulling rate and the heater temperature with dropped decreasing rate, and the crystal shape as well as the corresponding process could be designed by the method proposed in this paper. A suggested process design strategy is designing the pulling rate according to the given crystal shape and the pre-determined heater temperature.

One point needs to be noted is that the one dimensional crystallization process whose quantity kinematical relation has been adopted in this paper is a approximation of a practical crystal growth by pulling since which, accurately speaking, is a quasi-directional crystallization process with three dimensional heat diffusion. Thus, the numerical method proposed in this paper should be considered as a preliminary process design method to reduce the design time, and further process optimization is still necessary for growing a desired shape crystal.

[1] E. Buehler, The First Czochralski Silicon, in: R.S. Feigelson (Ed.), 50 Years Progress in Crystal Growth: A Reprint Collection, Elserver. B.V, Amsterdam, 2004.

[2] D.F. Bliss, Evolution and Application of the Kyropoulos Crystal Growth Method, in: R.S. Feigelson (Ed.), 50 Years Progress in Crystal Growth: A Reprint Collection, Elserver. B.V, Amsterdam, 2004.

[3] F.J. Bruni, Interface Stability and Its Impact on Control Dynamics, in: H.J. Scheel, P. Capper (Eds.), Crystal Growth Technology, Wiley-VCH, Weinheim, 2008, pp. 267-281.

[4] N. Min, Physical Fundamentals of Crystal Growth, Shanghai Scientific and Technical Publishers, Shanghai, 1982.

[5] G. Singh, B. Ghosh, R.Y. Deshpande, On the Shape of Crystals Grown by Kyropoulos Technique, Kristall und Technik, 16 (1981) 1239-1245.

[6] K.C. Zhang, L.H. Zhang, Science and Technology of Crystal Growth, 2 ed., Science Press, Beijing, 1997.

[7] L.Y. Zhang, H.B. Zuo, J.F. Sun, X.H. Wang, J.C. Han, D.W. Xing, Theoretical Analysis of the Shape Evolution of Crystal Grown by Pulling, Crystal Research and Technology (2011).

[8] L.Y. Zhang, H.B. Zuo, D.W. Xing, J.C. Han, J.F. Sun, Quantitative Process Design of 1-D Crystallization for Pure Melt, Met. Mater. Int., 16 (2010) 725-730.

[9] J. Han, S. Meng, H. Zuo, M. Zhang, Large Sapphire Growth Technique with Micro-Pulling and Shoulder-Expanding at Cooled Center, State Intellectual Property Office China, 2006, p. 5.

[10] S.E. Demina, E.N. Bystrova, M.A. Lukanina, V.M. Mamedov, V.S. Yuferev, E.V. Eskov, M.V. Nikolenko, V.S. Postolov, V.V. Kalaev, Numerical Analysis of Sapphire Crystal Growth by the Kyropoulos Technique, Opt. Mater., 30 (2007) 62-65.

[11] C.-W. Lu, P.-H. Chi, 3d Simulation of the Effects of Growth Parameters on the Growth of Sapphire Crystals Using Heat Exchanger Method, Crystal Research and Technology, 42 (2007) 1259-1265.

[12] C.-W. Lu, J.-C. Chen, Numerical Computation of Sapphire Crystal Growth Using Heat Exchanger Method, Journal of Crystal Growth, 225 (2001) 274-281.

[13] C.H. Xu, Investigation of Simulation Analysis and Its Aoolication for the Growth of Large Size Sapphire with Sapmac Method, Ph.D Thesis of Harbin Institute of Technology Harbin, 2007.

Figure captions

Fig.1 Geometric relation between v and $v_{//}$

Fig.2 Sapphire crystal growth with on-line adjusting pulling rates, where T_H=2500K. a) Process curve of pulling rate ; b) $v_{//}$-t curve; c) Crystal shape;

Fig.3 Sapphire crystal growth with on-line adjusting T_H, where u=1μm/s. a)T_H-t curve; b) $v_{//}$-t curve; c) Crystal shape;

Fig.4 Shapes of crystal grown under process conditions shown in Fig.3 but the heater temperature T_H is further required to be higher than the melt point T_C=2323K of sapphire crystal

Fig.5 Sapphire crystal growth with on-line adjusting both the heater temperature and pulling rate (T_H>2323K). a) T_H-t curve; b) u-t curve; c) $v_{//}$-t curve; d) Crystal shape; e) 3-D morphology of the crystal grown under condition T_H=2500-3t K, u=U1 ; f) 3-D morphology of the crystal grown under condition T_H=2500-3t K, u=U2.

Fig.6 3D shape of a designed crystal and the corresponding slop curve of its shape

Fig.7 Designed pulling rate curve, b), for growing the crystal designed in Fig.6 with a pre-determined heater temperature curve, a).

Fig.8 Designed heater temperature curve, b), for growing the crystal designed in Fig.6 with a pre-determined pulling rate curve, a).

Fig.1

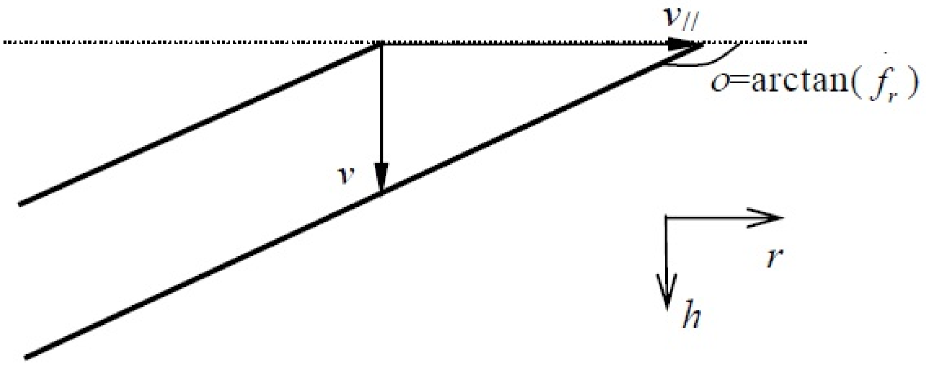


Fig.2

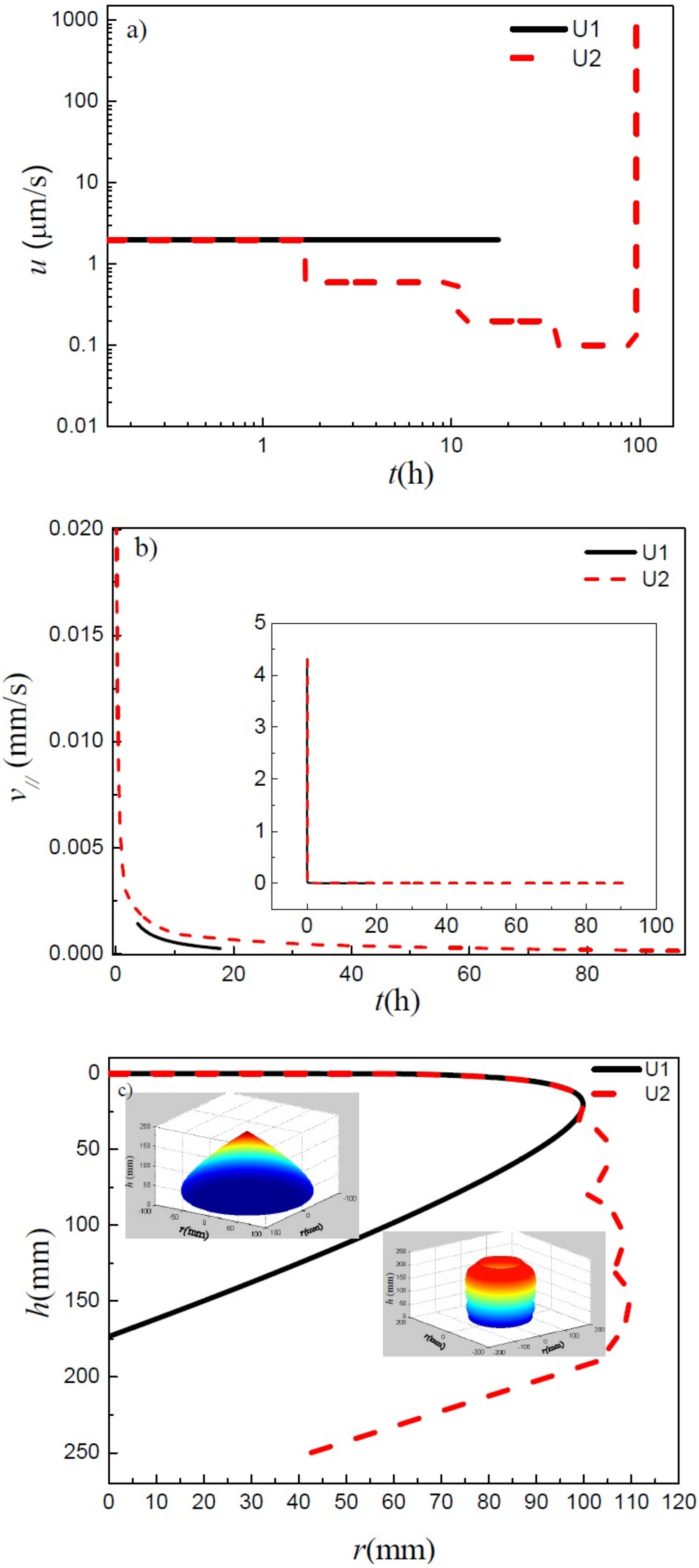
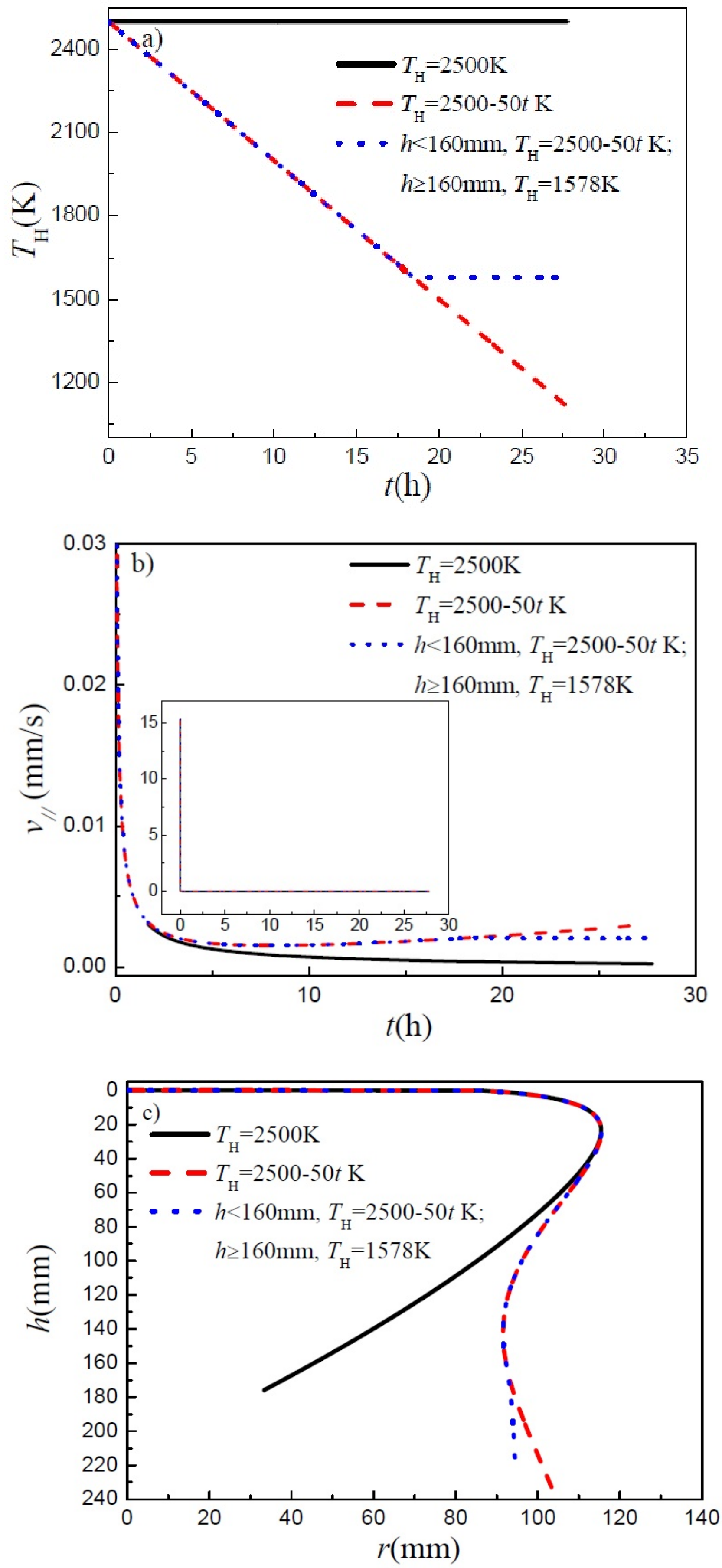
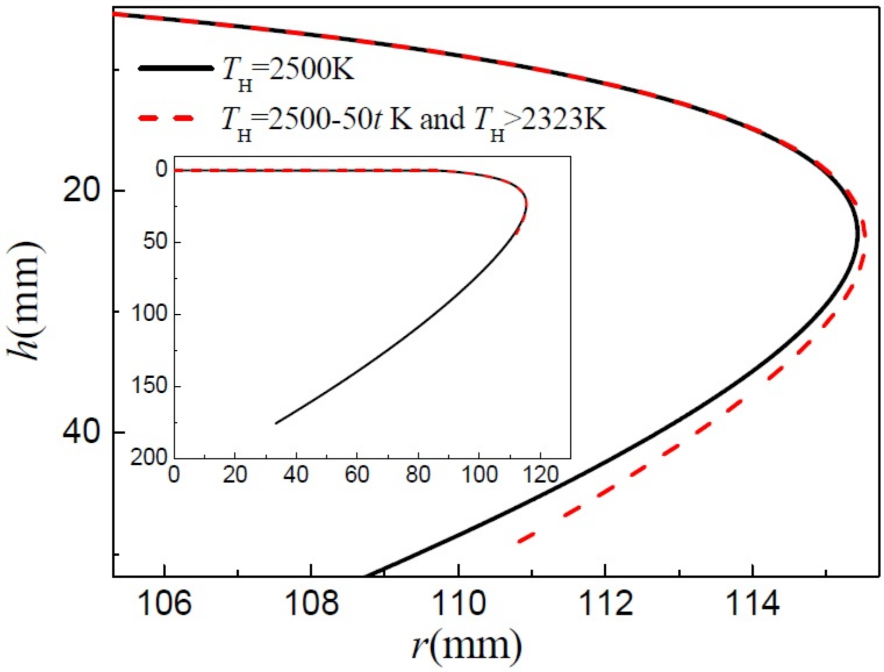

a)
U1
U2
u (μm/s)
1000
100
10
1
0.1
0.01
1
10
100
t(h)
b)
U1
U2
v// (mm/s)
0.020
0.015
0.010
0.005
0.000
0
20
40
60
80
t(h)
5
4
3
2
1
0
0
20
40
60
80
100
c)
U1
U2
h(mm)
0
50
100
150
200
250
0
10
20
30
40
50
60
70
80
90
100
110
120
r(mm)

Fig.3



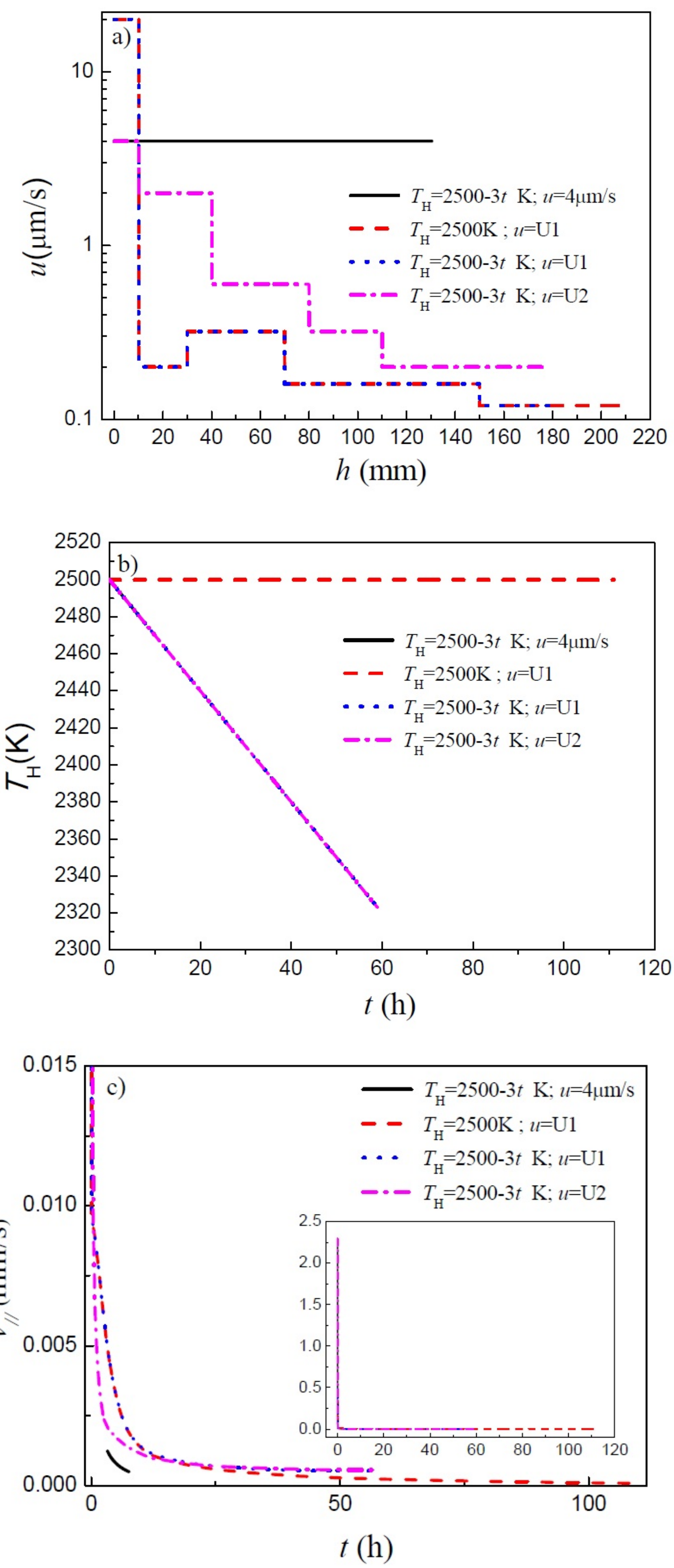
a)
T_H=2500K
T_H=2500-50t K
h<160mm, T_H=2500-50t K;
h≥160mm, T_H=1578K
T_H(K)
t(h)
b)
T_H=2500K
T_H=2500-50t K
h<160mm, T_H=2500-50t K;
h≥160mm, T_H=1578K
$v_{//}$ (mm/s)
t(h)
c)
T_H=2500K
T_H=2500-50t K
h<160mm, T_H=2500-50t K;
h≥160mm, T_H=1578K
h(mm)
r(mm)

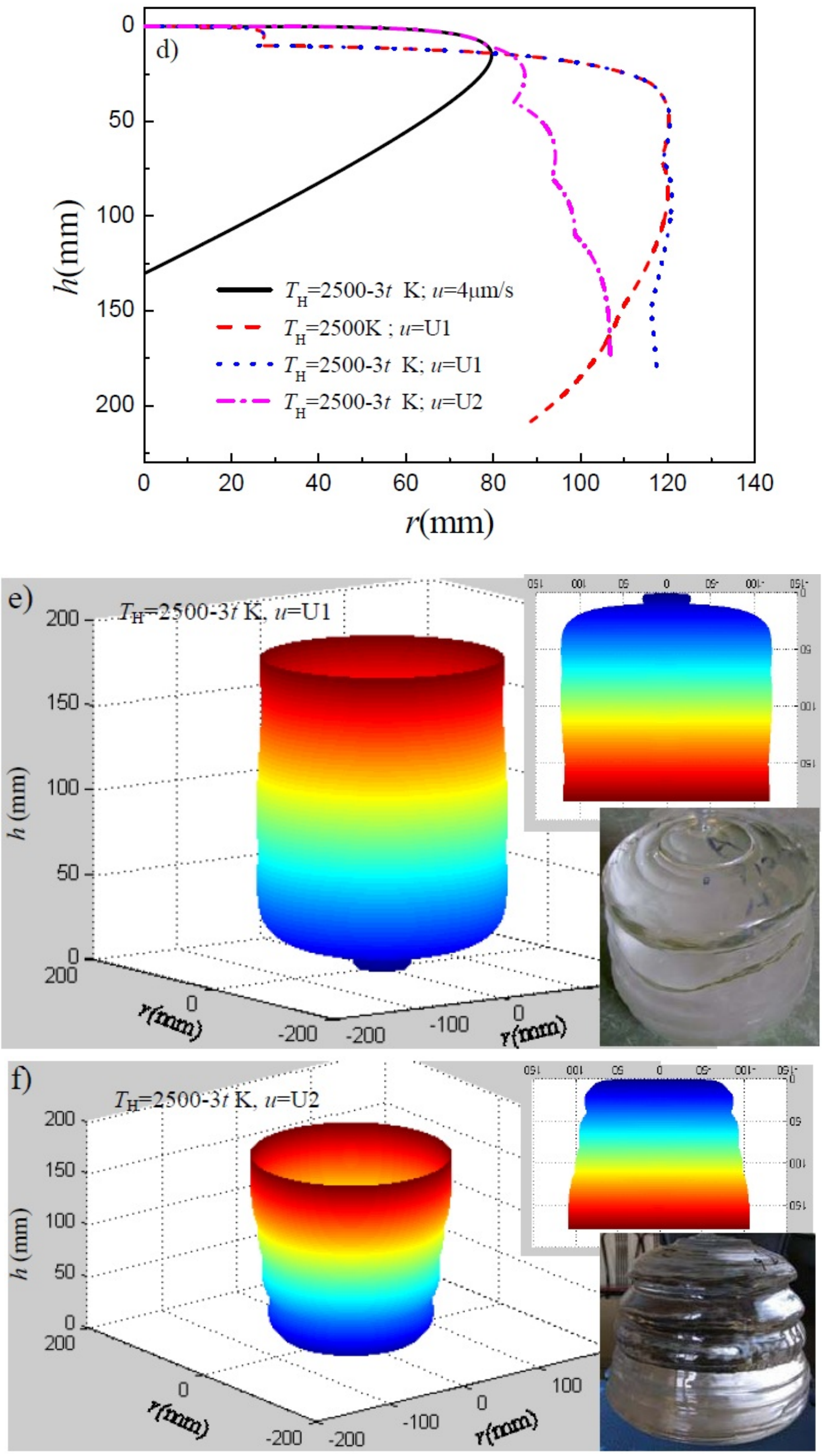
Fig.4



T_H=2500K
T_H=2500-50t K and T_H>2323K
h(mm)
r(mm)
20
40
106
108
110
112
114
0
50
100
150
200
0
20
40
60
80
100
120

Fig.5


a)
u(μm/s)
h (mm)
T_H=2500-3t K; u=4μm/s
T_H=2500K ; u=U1
T_H=2500-3t K; u=U1
T_H=2500-3t K; u=U2
b)
T_H(K)
t (h)
T_H=2500-3t K; u=4μm/s
T_H=2500K ; u=U1
T_H=2500-3t K; u=U1
T_H=2500-3t K; u=U2
c)
v_// (mm/s)
t (h)
T_H=2500-3t K; u=4μm/s
T_H=2500K ; u=U1
T_H=2500-3t K; u=U1
T_H=2500-3t K; u=U2



d)
h(mm)
r(mm)
T_H=2500-3t K; u=4μm/s
T_H=2500K ; u=U1
T_H=2500-3t K; u=U1
T_H=2500-3t K; u=U2
e)
T_H=2500-3t K, u=U1
h (mm)
r(mm)
f)
T_H=2500-3t K, u=U2
h (mm)
r(mm)

Fig.6

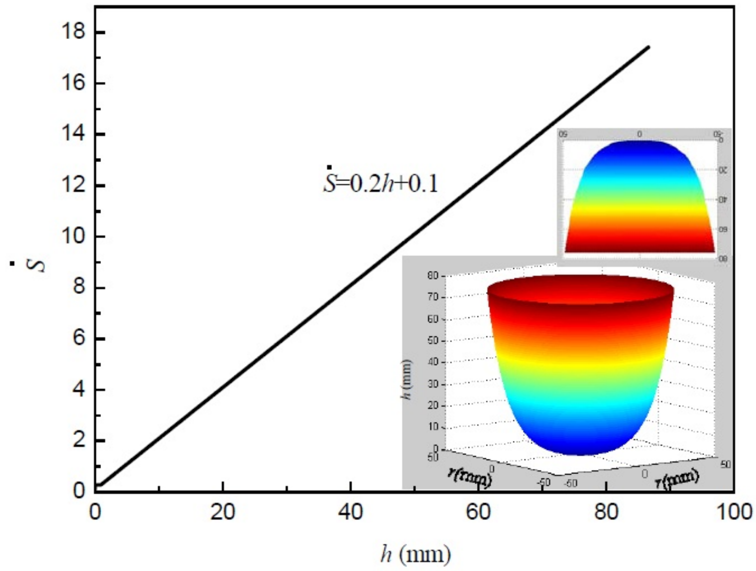
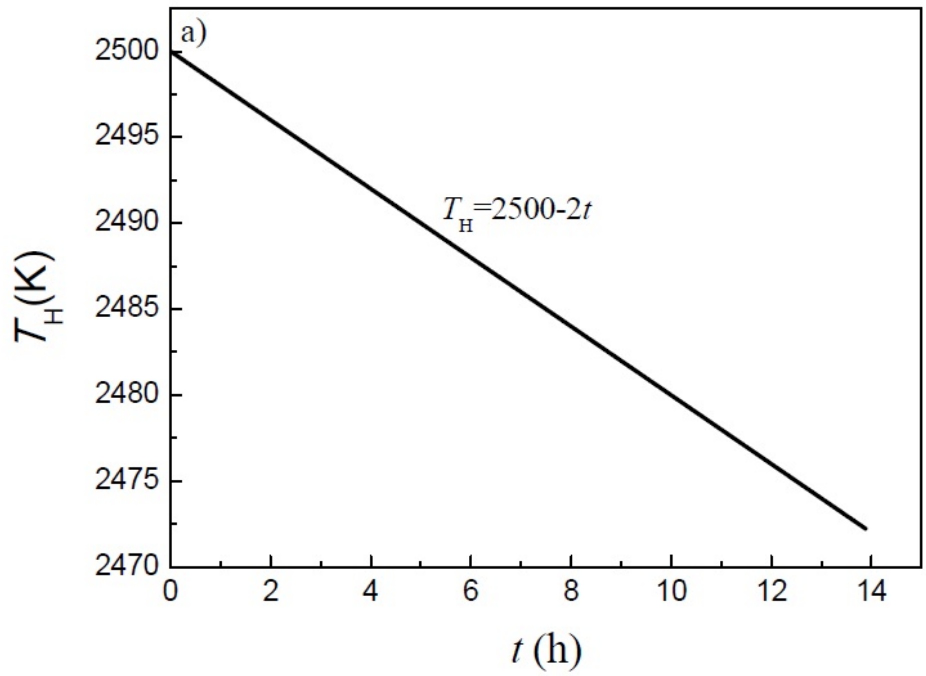
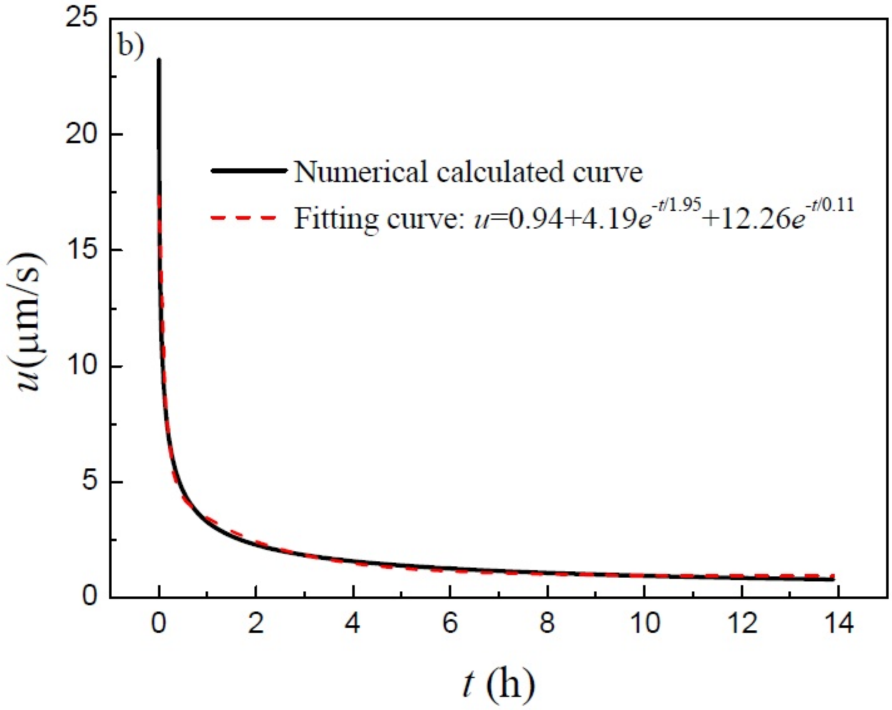


Fig.7



a)
T_H=2500-2t
2500
2495
2490
2485
2480
2475
2470
T_H(K)
0
2
4
6
8
10
12
14
t (h)



b)
Numerical calculated curve
Fitting curve: u=0.94+4.19$e^{-t/1.95}$+12.26$e^{-t/0.11}$
25
20
15
10
5
0
u(μm/s)
0
2
4
6
8
10
12
14
t (h)

Fig.8