

EFFECTS OF TENSILE STRESS AND IMPURITIES ON CREEP ACTIVATION ENERGY OF PLATINUM^①

Mu, Jialong He, Huachun

Institute of Precious Metal, Kunming 650221, China

ABSTRACT

The effect of tensile stress and trace amounts of impurities on the creep activation energy of platinum was studied and the creep mechanism was discussed.

Key words: tensile stress creep activation energy platinum creep mechanism

1 INTRODUCTION

The effect of tensile stress on the creep time curve can be described by the formulae as follows^[1].

High tensile stress;

$$\dot{\epsilon} = A \cdot \exp[-(Q_0 - a\sigma)/RT]$$

Low tensile stress;

$$\dot{\epsilon} = B\sigma^n \cdot \exp(-Q/RT)$$

where $\dot{\epsilon}$ —creep rate;

Q —creep activation energy;

Q_0 —initial creep activation energy

without tensile stress;

A, B, a, n —constants.

Most researchers have proved that the initial creep activation energy of metal is its self-diffusion activation energy. The effect of tensile stress on creep activation energy of platinum was studied by Carreker^[2]. There was no simple linear relationship between Q and σ . Q_0 was between 284.7 kJ/mol and 326.6 kJ/mol which was corresponding to the self-diffusion activation energy of platinum. Later, the creep features of Pt, Al, Ni and Zn were studied by Жыркоб. In the results, the creep time curve fitted the formula(1). Q decreased linearly with σ , that

is $Q = Q_0 - a\sigma$. In the case of Pt, Al, Ni, Q_0 approximated to the heat of evaporation of the metal as the tensile stress approached zero. So the doubt of common means of the creep mechanism of diffusion was caused.

The paradox above has not been resolved reasonably since then. For this reason, the effect of tensile stress and trace amounts of impurities on creep activation energy of platinum is studied in this paper. The results show that at low tensile stress, Q_0 increased rapidly with the decreasing σ and was independent to the tensile stress; and trace amounts of impurities have great influence on Q_0 . The paradox discussed for a long time was explained and resolved with interstitial mechanism of self-diffusion.

2 EXPERIMENTAL METHOD

The purity of platinum for P—1 and P—2 are 99.99% and 99.95% respectively. The Pt—RE alloys are made from Pt—(P—2) and RRE (La, Pr, Nd, Lu, Sc, etc.) with the purity of 99.99%. The metal powder was mixed and pressed, then placed in Al_2O_3 crucible with high purity and melted

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in high frequency furnace with the protect of Ar gas and under 10^{-3} mm Hg vacuum. The wire of foil for testing sample were made by general working methods.

The spectrographic analysis was used to analyze the composition of fine wire and the main impurities in P—1 and P—2 were shown in Table 1.

Table 1 The main impurities of platinum

Samples	impurities elements					
	Si	Ca	Al	Pd	Rh	Ir
P—1	0.05	0.03	0.0059	<0.00030	0.0018	0.001
P—2	0.05	0.03	0.0010	>0.01	0.0012	0.022

The amounts of other impurities, such as Cu, Ag, Mg, Pb, Fe, Zn and B, in both P—1 and P—2 are almost the same and the average amount was less than 0.004%. The contents of Au, Fe in P—2 was slight higher than in P—1.

The self-made apparatus was used for creep testing. The apparatus consists three parts: stand-pipe furnace body (SIC), dangling and loading of sample, time clock and temperature control system. The length of uniform temperature region in the furnace was 30 mm, and temperature varied between ± 3 °C. Sample is 130 mm in length and 0.3 mm in diameter. The upper and down sample hook was made of Pt—Rh30 alloy which connected with time clock. Temperature of furnace was automatically precisely controlled by the JWT—702 with a PtRh₆—PtRh₃₀ thermal couple. A Pt—PtRh10 thermal couple and UJ27 apparatus were used to measure temperature.

3 RESULTS

Under 10 MPa tensile stress, the relation of creep rupture time and temperature of sample fitted the formula(1). At the tem-

perature of 1 200 ~ 1 400 °C, the creep curves of PtLa_{0.01} and PtLu_{0.01} are straight lines, but the creep time curve of P—1 and P—2 is refractive line. The refractive point is at 1 300 °C. The values of creep rupture activation energy are shown in Table 2. At the temperature of 1 300 ~ 1 400 °C, Q of platinum is higher than that of 1 200 ~ 1 300 °C, and the creep rupture energy of Pt decreased when trace amounts of impurities was added. This is because that Pt and rare earth formed into single phase alloy^[4].

Fig. 1 shows the effect tensile of stress on creep time. The curve of $\lg \sigma - \lg t$ fits formula(2). Under 10 MPa tensile stress, the creep curve is a straight line. When $\sigma > 10$ Mpa, the curve bends down and changes into two refractive lines, with n increasing. The curve of $\lg \sigma - \lg t$ of PtLa_{0.01} and PtLu_{0.01} are similar with that of Pt, the value of n increased with the amount of rare earth. At low tensile stress the curve of $\lg \sigma - \lg t$ bends upward, n is even higher, this is caused by inner oxidation.

Table 2 The creep activation energy(Q) and n of platinum

samples	Q (10 MPa) /kJ·mol ⁻¹	T / °C	n (1 200 °C)	
			$L\sigma$	$H\sigma$
P—1	344.6	1 200 ~ 1 300	3.9	7.6
	521.7	1 300 ~ 1 400		
P—2	318.6	1 200 ~ 1 300	4.2	5.6
	454.3	1 300 ~ 1 400		
PtLa _{0.02}	260.4	1 200 ~ 1 400	6.6	4.3
PtLa _{0.01}	281.4	1 200 ~ 1 400	3.7	4.62
PtLu _{0.03}	241.2	1 200 ~ 1 400	2.3	4.5

The creep curve of P—1 and P—2 were tested at the temperature of 1 200 °C ~ 1 300 °C as tensile stress changed from 3 to 20 MPa, and Q was calculated using formula

(1). The value of Q increased obviously with the decrease of σ as σ less than 7 Mpa. The bent-down curve in Q - σ diagram is different from (3) or (2). The curve of Q - $\lg\sigma$ drawn with tested data was two straight line (Fig. 1). So the relation of activation energy and tensile stress was described as formula: $Q = Q_0 - c \ln\sigma$.

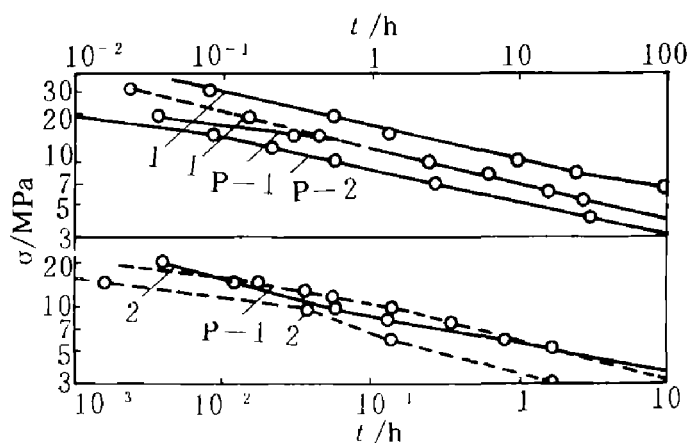


Fig. 1 The relation of creep rupture time(t) and tensile stress(σ_t)

1—PtLa_{0.22}; 2—PtLu_{0.05}

solid line—1200 °C; dash line—1300 °C

At low tensile stress, both straight lines of P—1 and P—2 approached the point of 122 kJ·mol⁻¹ as the σ got near to zero, which corresponds to the heat of evaporation of platinum. At high tensile stress, the value of Q of P—2 equals to 320.3 kJ·mol⁻¹, which correspond to activation energy of self-diffusion of platinum. The value of Q_0 of P—1 is even higher. The creep rupture activation energy of PtLa, PtLu, PtSc alloys, etc., were also tested in the same way, some of the typical curves of Q - $\lg\sigma$ were shown in Fig. 2. At high tensile stress, the variation of Q with σ for PtLa alloy is similar with that of Pt, but Q of PtLu, PtSc alloys appear some irregular changes. At low tensile stress the value of Q increase sharply with the decrease of σ in Pt-RE alloys, its changing rate is greater than in Pt.

The initial creep activation energy of Pt and Pt-RE alloys, the activation energy of self-diffusion of Pt(Q_D), the heat of evaporation Q_s of Pt are listed in Table 3.

Table 3 The activation energy and heat of evaporation for Pt and Pt-RE

sample	$Q_0(H\sigma)/$ kJ·mol ⁻¹	$Q_0(L\sigma)/$ kJ·mol ⁻¹	$Q_s/$ kJ·mol ⁻¹	$Q_D/$ kJ·mol ⁻¹
P—1	389.4	510.8	531.7	314
P—2	320.3	510.8	531.7	314
PtLa _{0.22}	325.3	2219.0		
PtLa _{0.01}	322.4	665.7		
PtLu _{0.03}		873.2		
PtLu _{0.05}		1582.6		

It can be seen from Table 3 that at high-tensile the values of Q_0 of P—2 and PtLa alloy containing trace amounts of rare earth are equal to the activation energy of self-diffusion of Pt. At low tensile stress, the Q_0 of P—1 and P—2 approximate the heat of evaporation of Pt, the Q_0 of Pt-RE alloys is higher than the heat of evaporation of Pt, and increase sharply with the composition of rare earth.

4 DISCUSSION

At high tensile stress initial creep activation energy of Pt and Pt-RE alloys approximate the activation energy of self-diffusion of Pt as tensile stress got near to zero. From this, it can be concluded that the creep mechanism of Pt and its alloys is controlled by the mechanism of vacancy diffusion. At high tensile stress the creep rupture time is very short. So no inner oxidation in the sample occurred. The atom of element of impurities were solid soluted in Pt as the model of insteading of atom of Pt. At high tempera-

ture, creep metal with high purity and alloy of single phase have bigger dislocation network, which caused little curb of interstitial structure. So there are enough vacancy in crystal for dislocation to move with the way of absorbing vacancy. Thus, the creep activation energy is equal to the activation energy of vacancy self-diffusion. The creep deformation of sample was caused by the increase of dislocation.

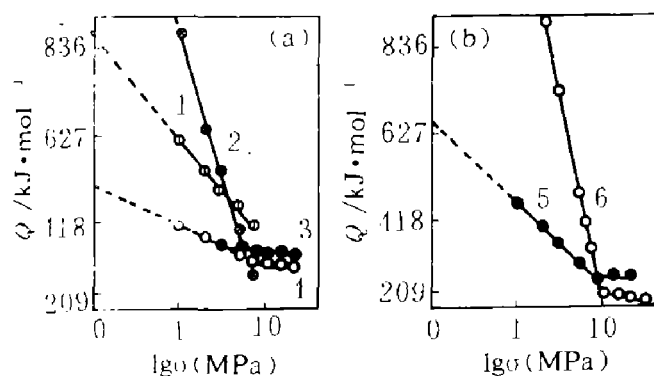


Fig. 2 The relation of creep rupture activation energy and tensile stress

1—PtLu_{0.03}; 2—PtLu_{0.05}; 3—P—1;
4—P—2; 5—PtLa_{0.01}; 6—PtLa_{0.02}

At the range of low tensile stress. The creep rupture activation energy of platinum and PT-RE alloys increase rapidly with the decrease of tensile stress. The value of Q_0 for Pt approximate its heat of evaporation as tensile stress got near to zero. Although this phenomenon was observed early, it has not been explained very clearly by now. The effect of impurities are therefore studied in the paper. The solubilities of other precious metals and most transition metal in platinum are higher than that of Si, Ca, Mg, Al and rare earth elements. When trace amounts of impurities added, the effect of the former on activation energy of platinum was less than that of the later. This effect would be greater if Si, Ca, Al and RE formed into dioxided particle in platinum.

The creep rupture time was very long

at low tensile stress. It is sufficient for Si, Ca, Al and rare earth elements to form their steady dioxides. In this kind of dispersed alloy, the dislocation network was very small in the process of deformation, and recovery during the creep. In the movement of dislocation this network cross-cuts with the screw dislocation resulting relative more interstitial atomic curb. Because There is not much vacancy in crystal, the atomic curb can't move as the model of absorbing vacancy but give out the interstitial atom. Thus, the creep activation energy equals to the activation energy of interstitial self-diffusion.

The results were obtained from spectrographic analysis. The content of Si among the impurities in platinum is the highest and Ca the second. The atomic radius of Si approximate that of Pt. The radii of Ca and rare earth elements are at least 15% larger than that of Pt. It is quite different from the interstitial solid resolution with small radius. For the sake of creep, radiation and cool harden working etc., some of the atoms displaced from original position and entered into the interval of crystal lattice to form another kind of interstitial solid resolution. In these kinds of displaced alloys or pure metals great energy is needed to form some interstitial atom. It was difficult to calculate the activation energy on theory by now. The deformation of pure gold at the range of 42~520 K was studied by Shimonrura, Kino^[5]. In their research the interstitial atom was indeed caused. The interstitial atoms are few because of the need for high energy to form.

The radius of Al is 2% larger than that of Pt, and easy to form into steady particles of Al₂O₃. The existence of Al₂O₃ particle has great influence on the value of activation energy. From above data, the content of Al in P—1 is higher than that in P—2.

P—1 forms into "dispersed hardening" metal at high temperature. So the Q of P—1 at high tensile stress is greater than that of P—2.

In the mid-temperature creep, the important factor is the cross-cut slide of screw dislocation produced in the heat activation of process. The relation between activation energy of cross-cut slide (E) and tensile stress was described as follows:

$$E = E_0 - c \ln(N \cdot \tau / \tau_0) \quad (4)$$

where N —amount of dislocation per slide line unit;

τ_0 —transverse stress on the cross-cut slide surface;

C —constant

Comparing formula (3) with (4), we can find that they are very similar. So formula (4) can also be used in the case of high temperature. It is probably due to the decrease of fault energy of Pt caused by element of impurities.

5 CONCLUSIONS

(1) At high tensile stress, the initial creep activation energy of P—2 and PtLa single phase alloys are corresponding to the

activation energy of self-diffusion of Pt.

(2) At low tensile stress the value of Q_0 of Pt approximate to the Q_s of Pt, Q_0 of Pt-RE alloys are more greater than Q_s of Pt, and increasing the content of rare earth elements in alloys increases the activation energy of the alloys.

(3) The impurities of producing interstitial atom must have big atom radius, small degree of resolution and can form into steady dioxides. For the sake of such kinds of impurities, the activation energy can approximate the heat of evaporation of pure metal of even larger than that.

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