Creep Behavior of In Situ Synthesized 7715D Titanium Matrix Composite
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TiB and TiC reinforced titanium matrix composite was in situ synthesized by consumable vacuum arc remelting and hot-forging based on reaction between titanium, B4C powder and graphite powder. The phases were analyzed through X-ray diffraction. The microstructure was examined by means of optical microscopy (OM) and scanning electron microscopy (SEM). Creep behavior was tested at three temperatures: 600 °C, 650 °C and 700 °C respectively within a stress range 100–350 MPa. Class I solution behavior was observed and true stress exponent \( n = 3.5 \) was obtained for the composite. Threshold stress, load transfer and micro-structural strengthening are considered for reasonably explaining the creep behaviour. It is concluded that strengthening mechanism can be owed to co-effect of all the three factors. True activation energy equal to 343 kJ/mol was obtained after compensation by threshold stress. [doi:10.2320/matertrans.MRA2008425]

(Received November 13, 2008; Accepted March 4, 2009; Published May 25, 2009)

Keywords: composite material, creep, microstructure, scanning electron microscopy (SEM)

1. Introduction

The search for alloys with improved high temperature specific strength and creep-resistant properties for aerospace applications has led to sustained research activities in the last decades. In these activities, titanium based alloys are developed as structural materials for engine of aircraft, aerospace components, hydrogen storage materials and shape memory alloys due to their low density, high strength and modulus, corrosion resistance and other eminent properties. In spite of these advantages, applications of Ti alloys are still limited by high temperature. For higher serving temperature of Ti alloys, some alloying elements and ceramic reinforcements are added to fabricate titanium matrix composites (TMCs) in order to improve the mechanical properties under high temperature. TiB and TiC are always considered to be the best reinforcements because of good combination with Ti matrix, high thermal stability and similar density to titanium. So far most matrix alloys of TMCs are compounded through addition of alloying elements such as Si, Nb or Zr based on Ti-Al-Sn-Mo-V system with variable element ratio. 7715D high temperature Ti alloy is one of these alloys, which is mainly developed for aviation and spaceflight and belongs to Ti-Al-Sn-Zr-Nb-Mo-Si-Ce system. Now in situ technologies has been used to synthesize TMCs with better mechanical properties than traditional processing methods, because the reinforcements are fine and thermodynamically stable, and the matrix-reinforcement interfaces are less polluted and better compatible.

In this work, 2% (volume fraction) TiB and TiC (mole ratio 1:1) reinforced TMC was synthesized by in situ technologies to improve high-temperature properties of 7715D Ti alloys based on the reaction among titanium, its alloyed elements, B4C powder and graphite powder as following equations:

\[
5\text{Ti} + B_4\text{C} \rightarrow 4\text{TiB} + \text{TiC} \quad (1)
\]

\[
\text{Ti} + \text{C} \rightarrow \text{TiC} \quad (2)
\]

Creep deformation property is one of the important indexes of high-temperature properties. Sherby, Burke and Cannon have pointed out that the creep behavior of solid solutions can be divided into two categories: Class I alloys whose creep behavior controlled by viscous dislocation sliding is different from pure metals and Class II alloys whose creep behavior controlled by dislocation climb is similar to pure metals. However, stress dependence of the steady-state creep strain rate of both solutions can be described by power law creep equation in certain stress and temperature range as follows:

\[
\dot{\varepsilon} = \frac{A\sigma^n}{\exp\left(\frac{-Q}{RT}\right)}
\]

\[
Q \text{ [kJ/mol]} = -R \frac{d \ln \dot{\varepsilon}}{d \frac{1000}{T}}
\]

where \( \dot{\varepsilon} \) is the steady-state creep rate of the material, \( \sigma \) is the applied stress, \( A \) is a constant related to material property, \( n \) is the stress exponent and \( Q \) [kJ/mol] is the activation energy. Strengthening mechanisms by reinforcements during steady state creep have been explained by two concepts: the first one is dispersion strengthening by fine reinforcements pinning the dislocation movement; the other concept is composite strengthening by load transfer into rigid reinforcements, and resulting in higher creep resistance than the matrix materials. Based on these two concepts, steady state creep was mainly studied in this work.

2. Experimental Procedure

For synthesizing TiB+TiC/Ti composite, Grade I sponge titanium, B4C powder, graphite powder, and samples for producing 7715D Ti alloy, such as Ti-Sn, Al-Ce, Mo powder or Al-Mo, sponge Zr, crystal Si and Nb powder, consisted of the raw materials. The above were blended according to a certain stoichiometric ratio and melted homogeneously in a consumable vacuum arc-melting furnace. The whole melting sequence was taken twice in order to make the inclusive difficult-melting alloys fully and well-proportioned diffuse and ensure chemical homogeneity. After casting, the
ingots were hot forged at 1080°C into square bars with a cross section of 30 mm × 40 mm rectangle. In succession, both the composite and the matrix alloy were heat-treated under the same condition: solution treatment (980°C/2 h/air-cooling) and annealing (570°C/4 h/air-cooling).

D-max-2250 V X-ray diffract instrument (XRD) with Cu as the target material under a 40 kV voltage was used to study the phrase in the composite. 10 mm × 10 mm × 10 mm cubic samples were cut from the heat-treated rods for optical microscopy. Specimens prepared by conventional grinding and polishing were non-etched for observing the reinforcements and etched with a solution of water, nitric acid, and hydrofluoric acid in cubage proportion of 7 : 3 : 1 for investigating the microstructure of the TMC and matrix alloy.

Specimens with a gauge dimension of 101 mm × 18 mm × 2 mm were machined along parallel of the hot-forging direction from the heat-treated rods for testing creep deformation behavior. Creep tests were conducted on a floor-mode CSS-3905 testing machine which has three-point temperature monitoring by thermocouples at the top, center, and bottom position of the specimens with fluctuations ±0.2°C. Creep properties of the composites and matrix alloy were respectively tested at 600°C, 650°C and 700°C within a stress range from 100 MPa to 350 MPa. A Philips SEM FEI SIRION 200 scanning electron microscope (SEM) with an applied 20 kV accelerating voltage was used to further work over the microstructure before and/or after creep deformation.

3. Results and Discussions

3.1 Initial microstructure

Figure 1 shows the X-ray diffraction patterns of the matrix and TMC. Based on the patterns, diffraction peaks of TiB and TiC are observed and it can be concluded that the reinforcements are successfully synthesized through the reaction.

Figure 2(a) shows distribution of the reinforcements by optical microscopy (OM) along the forging direction in the composite. TiB whiskers/dispersoids and TiC particulates uniformly disperse among the matrix. The reinforcements are so fine and small that it may contribute to pinning dislocations or undertaking load in creep deformation process. SEM is also used for observing the reinforcements after the sample was etched as shown in Fig. 2(b). TiB whiskers have an average width of about 1.5 μm and different length ranging approximately from 6 μm to 15 μm. TiC particulates have a near-equiaxed shape. Meanwhile, it can be observed that the reinforcements hold well combination with the matrix.

Microstructure of both the matrix and the composite are shown in Fig. 3. As shown in Fig. 3(a), the matrix alloy displays a coarse colony microstructure of similarly aligned Widmanstatten α + β phrase. Some primary α phrases still exist at the grain boundaries. The composite in Fig. 3(b) displays a microstructure consisting of fine Widmanstatten α + β lath matrix with reinforcements homogeneously dispersing in it.

3.2 Creep behavior of steady-state stage

Figure 4 shows the creep curves and corresponding strain-rate vs. time curves of the matrix alloy and composite. Different from the typical curves of Class II solid solutions, some curves here present the rate-increasing stage of Class I solid solutions before the steady-state creep stage, as obviously shown in Figs. 4(a) and 4(b). The corresponding
strain-rate vs. time curves are shown in Figs. 4(a) and 4(b), respectively. Other curves show inconspicuous or no steady-state stage, as shown in Figs. 4(c) and 4(d) with the corresponding stress-rate vs. time curves respectively in Figs. 4(c’) and 4(d’). For the latter situation, the lowest creep strain rate is used as steady-state creep rate.

Table 1 shows the steady-state creep rate at all test conditions. In comparison with the matrix alloy, creep resistance of the TMC is actually enhanced due to addition of the reinforcements. The stress dependence of steady-state creep strain rate for the matrix alloy and TMC is shown on a double logarithmic scale in Fig. 5. Apparent stress exponents of the matrix alloy are 3.47, 3.57 and 3.05 respectively at 600°C, 650°C and 700°C. They all belong to the range 3.0–3.5 of Class I solid solutions where diffusion controlled viscous dislocation slide is considered as the creep mechanism. This result is different from H. Hofmann’s11 research on Ti-12Co-5Al and Ti-10Co-4Al. In his work, it was pointed out that stress exponent of n = 3.5 could be achieved at low stress level of 80–100 MPa, which is lower than 150–300 MPa of the present work within the temperature range 600°C–650°C. Oikawa et al.12,13 also indicated that the stress exponent of 3.5 implies that Class I behaviour is dominant at low stress level, but at higher stress level the stress exponent is 4.6 where Class II is governing. It was also pointed out that the transition depends on the temperature and increases with increasing aluminum. So the distinction can be attributed to the high Al content of 7715D alloy (close to 7) and high measure temperature. The transition from Class II to Class I solution behaviour may occur in such case. It also explains the special behavior of the creep curves.

The apparent stress exponents of TMC are higher than those of the matrix alloy and possess a decreasing trend with temperature increasing. If the shear modulus is considered, the specific behavior of the creep curves.

Table 1 Steady-state creep strain rate of the matrix alloy and TMC at different test conditions.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Stress (MPa)</th>
<th>Matrix alloy (s⁻¹)</th>
<th>TMC (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>200</td>
<td>1.02 × 10⁻⁸</td>
<td>6.19 × 10⁻⁹</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>5.41 × 10⁻⁸</td>
<td>3.27 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>6.48 × 10⁻⁸</td>
<td>5.53 × 10⁻⁸</td>
</tr>
<tr>
<td>650</td>
<td>150</td>
<td>5.93 × 10⁻⁸</td>
<td>3.82 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>2.00 × 10⁻⁷</td>
<td>1.46 × 10⁻⁷</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>7.20 × 10⁻⁷</td>
<td>5.82 × 10⁻⁷</td>
</tr>
<tr>
<td>700</td>
<td>100</td>
<td>2.11 × 10⁻⁷</td>
<td>8.23 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>6.45 × 10⁻⁷</td>
<td>5.48 × 10⁻⁷</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.77 × 10⁻⁶</td>
<td>1.21 × 10⁻⁶</td>
</tr>
</tbody>
</table>

where \( \dot{\varepsilon} \) is the steady-state creep rate of the material, \( \sigma \) is the applied stress, \( A \) is a constant related to the material property, \( n \) is the stress exponent, \( Q \) [kJ/mol] is the activation energy, \( G \) is the shear modulus of alpha titanium, \( R \) is the gas constant, \( T \) is the Kelvin temperature, and \( D \) is the diffusion coefficient which fits the Arrhenius relationship with the temperature. According to eqs. (3) and (5), the activation energy can be determined by the Arrhenius plot of logarithmic \( \dot{\varepsilon} \) or \( \dot{\varepsilon}T^m \) versus the reciprocal Kelvin temperature \( 1000/T \) at constant stress.

Figure 6 shows the Arrhenius plot of logarithmic \( \dot{\varepsilon} \) versus the reciprocal Kelvin temperature 1000/T. The apparent activation energies of the matrix at 150–300 MPa calculated according to eq. (3) belong to the range 347–365 kJ/mol and the values are lower than those of the composite (374–398 kJ/mol). All these values are much higher than 240 kJ/mol of the self diffusion usually reported for \( \alpha \) Ti.15 However, the values are close to 329 kJ/mol, the activation energy for Al diffusion in \( \alpha \) Ti pointed out by Koepper et al.16 The result is consistent with the Class I type creep mechanism presented above, for which the drag effect of solute on the creep process is very great. Considering the other main impurities in this alloy matrix, Zr belongs to the ‘normal’ impurities as well as Al in \( \alpha \) Ti according to Y. Mishin and C. Herzog.17 They pointed out that this type of impurities has close diffusion coefficients to the self-diffusion of \( \alpha \) Ti within approximately an order of magni-
Fig. 4 Creep deformation curves and corresponding strain rate vs. time curves of matrix alloy at (a)/(a') 600°C, (c)/(c') 700°C and TMC at (b)/(b') 600°C, (d)/(d') 650°C. (Symbol “×” means interruption of creep test).
and Nb in \(\alpha\) Ti, Nakajima and Koiwa\(^{18}\) pointed out that the diffusivity of the impurities have correlation with their atomic sizes and solubility. The smaller atomic size than Ti and the lower solubility in \(\alpha\) Ti may induce the impurity to diffuse faster. Sn is bigger than \(\alpha\) Ti and Nb is close to \(\alpha\) Ti in atomic size, which makes substitutional impurity diffusion and good solubility more probable. In such case, the vacancy mechanism is believed to be operative and the diffusion coefficients of the impurity atoms are expected to be of similar magnitudes to that of solvent self-diffusion. Low content of these existences will not apparently increase the diffusion coefficient or decrease the activation energy for the creep. Actually the measured activation energy reflects integrative drag effect of all solute elements, not just of Al element.

3.3 Threshold stress of the composite

Threshold stress theory is usually used to explain the higher apparent stress exponents of the composite. A simple method can be introduced to determine the threshold stress by utilizing the power law creep relationship eq. (3) and extrapolating the baseline of the \(\dot{\varepsilon}^{1/n}\) versus \(\sigma\) plots to \(\dot{\varepsilon}\) equal to zero. It requires the value of the true stress exponent \(n\) that is often assumed to be equal of that for the matrix.\(^{19}\) Though in present research \(n\) values of the matrix differentiate from each other, they are all close to 3.5 which is considered as the typical value for Class I solid solution according to H. Hofmann.\(^{11}\) As mentioned above, the creep curves of both matrix alloy and composite exhibit Class I solution behavior, so here 3.5 is used as the true stress exponent. Then this value is applied to calculate the threshold stress of the composite. It is also used to eliminate the measured aberration of the stress exponents for the matrix by linear plots of \(\dot{\varepsilon}^{1/3.5}\) versus \(\sigma\) through the origin point. Figure 7 shows good linear relationships, which indicate that it is rational to choose 3.5 as the true stress exponent of the composite. The threshold stress decreases from 30 to 10 MPa with the temperature increasing. Then stress dependence of the steady-state creep rate for the matrix and TMC at the three temperature levels can be expressed as follows (the subscripts of ‘c’ and ‘m’ in the following equation represent the composite and matrix alloy, respectively):

\[
\dot{\varepsilon}_c (600^\circ C)[s^{-1}] = 9.4174 \times 10^{-17}(\sigma[MPa] - 30)^{3.5}; \\
\dot{\varepsilon}_m (600^\circ C)[s^{-1}] = 9.3790 \times 10^{-17}(\sigma[MPa])^{3.5} \\
\dot{\varepsilon}_c (650^\circ C)[s^{-1}] = 1.5625 \times 10^{-15}(\sigma[MPa] - 18)^{3.5}; \\
\dot{\varepsilon}_m (650^\circ C)[s^{-1}] = 1.5810 \times 10^{-15}(\sigma[MPa])^{3.5} \\
\dot{\varepsilon}_c (700^\circ C)[s^{-1}] = 1.3604 \times 10^{-14}(\sigma[MPa] - 10)^{3.5}; \\
\dot{\varepsilon}_m (700^\circ C)[s^{-1}] = 1.6290 \times 10^{-14}(\sigma[MPa])^{3.5}
\]

True activation energies of the matrix and TMC can be recalculated after compensation with the threshold stress and regulation of the stress exponent of the matrix alloy. According to eq. (4) \(\dot{\varepsilon}\) is normalized as \(\dot{\varepsilon}\)\(_{TG}\)\(^{2.5}\). Figure 8 reveals the result of recalculation. At the same true stress level, the plots of the matrix alloy and TMC nearly superpose. Through calculation by eq. (5), the activation energies of all three stress levels are equal to 343 kJ/mol which is very close to 329 kJ/mol of Al solute diffusion in \(\alpha\) Ti mentioned above. The fine accordance between the matrix and composite indicates it is appropriate to use threshold stress to explain the strengthening mechanism.

Some possible mechanisms have been utilized to explain the origin of the threshold stress. There are mainly three

![Fig. 5](image1)

Stress dependence of the steady-state creep rate of matrix alloy and TMC on a double logarithmic scale.

![Fig. 6](image2)

Arrhenius plots of the logarithmic creep rate versus the reciprocal Kelvin temperature for the matrix and composite at different constant stress.

![Fig. 7](image3)

Threshold stresses of the composite at different temperature.
models according to Mohamed. In all these models, the threshold stress originates from: (1) the stress required to cause dislocation bowing between particles (the Orowan stress $\tau_o$); (2) the extra back stress required to create the additional dislocation line length as the dislocation segment climbs over a particle (local climb); (3) the stress required to detach the dislocation from the particle after climb is complete. Here in the present work, the Orowan stress can be estimated by using formula $\tau_o = \frac{G b}{\lambda}$, where $G$ is the shear modulus which can be expressed as $G = \frac{49500}{T}$ MPa, $b$ is the Burgers vector here equal to about $3 \times 10^{-10}$ m, and $\lambda$ is the average interspacing of the reinforcement particles and can be estimated through Fig. 2(a) as $35 \mu m$. Then after calculation at the testing temperatures, the Orowan stresses are all smaller than 0.3 MPa, which is much lower than the measured threshold stresses. It seems that Orowan stress relating to the reinforcements can’t be explained as the origin of the threshold stresses. Similarly, due to lower values than Orowan stress, models (2) and (3) cannot either be used for the reinforcements to explain the threshold stress. However, as Mohamed pointed out in his paper of review, fine incoherent oxide particles, as a consequence of composite fabrication, serve as effective barriers to the dislocation motion, and the result of calculation using model (3) is closely consistent with the experimental data. In this paper, although the details about the threshold stress are still unclear, it may correlate with the interactions between the dislocations and extremely finer particulates induced from the addition of reinforcements.

Figure 9 shows plots of the normalized creep strain rate versus the true stress compensated with the threshold stress of the composite on a double-logarithmic scale. Nearly all steady-state creep rates fall on the same straight line with a slope equal to 3.5 (representing the true stress exponent) at different temperatures. It means both creep mechanisms of the matrix and the composite are the same and no transition of creep mechanism occurred in the testing range.

### 3.4 Additional strengthening mechanisms in the composite

Though threshold stress theory can rationally explain the enhanced creep resistance of the composite, additional strengthening origins also can be considered. In present work, two factors except threshold stress are considered: (a) load transfer and (b) micro-structural strengthening.

Load transfer is observed in SEM of the composite crept at 600°C after more than 110 h. As shown in Fig. 10, TiB reinforcements crack in the middle due to taking load from the matrix. A coefficient $k$ can be introduced to express the effect of load transfer at an effective constant stress: $n = 3.5$ is the true stress exponent, and $\beta$ indicates load transfer effect from the matrix to the composite. The $\beta$ value lies between 0 (for the matrix without reinforcements) and 1 (load is completely transferred to the composite). From eq. (6) it can be observed that there are nearly no obvious distinctions of steady state creep rate between the matrix alloy and the composite under an effective constant stress at 600°C and 650°C, though load transfer was observed by SEM at 600°C. Actually, the values of $\beta$ calculated according to eqs. (6) and (7) at 650°C and 700°C are respectively 0.0004 and 0.005. The values are so small that load transfer cannot be considered as the main strengthening origin. The tendency

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Fig. 8 True activation energies after compensation with threshold stress.

Fig. 9 Plot of the steady-state creep rate normalized by diffusion coefficient and shear modulus versus the true stress compensated by shear modulus.

Fig. 10 SEM microstructure of the composite crept at 600°C/200MPa after more than 110 h.
that $\beta$ value increases with temperature increasing can be explained by shear-lag analysis according to L. Xiao.\(^1\) Using shear-lag theory, macro-stress of the composite and load transfer coefficient can be expressed as the following equations:

$$\sigma = E_r \varepsilon_0 \left[ 1 - \frac{\tan h(ps)}{ps} \right]$$  \hspace{1cm} (8)

$$\sigma_0 = \sigma_r \nu_r + \sigma_m \nu_m$$

$$= \varepsilon_0 \left[ \nu_r E_r \left[ 1 - \frac{\tan h(ps)}{ps} \right] + (1 - \nu_r) E_m \right]$$  \hspace{1cm} (9)

$$\beta = \frac{\sigma_r \nu_r}{\sigma_0} = \frac{\nu_r E_r \left[ 1 - \frac{\tan h(ps)/ps}{ps} \right]}{\nu_r E_r \left[ 1 - \frac{\tan h(ps)/ps}{ps} \right] + (1 - \nu_r) E_m}$$  \hspace{1cm} (10)

where $E_r$ and $E_m$ are elastic modulus of the reinforcements and the matrix, respectively, $\sigma$ is the average transferred stress, $\varepsilon_0$ is the strain, $\nu_r$ is the volume fraction of the reinforcements, $p$ and $s$ are parameters related to geometry of the reinforcements. $E_m$ decreases as temperature rises and $E_r$ changes little due to stiffness of the reinforcements. Other parameters, keep weak dependence on temperature. So it can be easily concluded from eq. (10) that $\beta$ increases as temperature rises. Also, it can be concluded that as temperature rises, threshold stress decreases but load transfer effect increases, and the strengthening origin switches from threshold stress to load transfer.

Micro-structural strengthening is another possibility for high creep resistance of the composite. Due to lower self and impurity diffusion in $\alpha$ Ti than $\beta$ Ti, the creep is controlled by deformation of $\alpha$ phase. The dislocation motions are always restricted in the main $\alpha$ phase in near $\alpha$ alloy. According to Bania and Hall,\(^2\) equiaxed $\alpha$ grained structure has lower creep strength than $\alpha/\beta$ lath structures, such as partly transformed $\beta$ grains and/or Widmanstätten microstructures. That is because $\alpha/\beta$ colony and lath boundaries can act as barriers to dislocation slip. The addition of the reinforcements in composite make the $\alpha/\beta$ colonies and laths more finer as shown in Fig. 3. The finer microstructure and lath structure can improve the creep resistance in the composite due to causing shorter dislocation slip lengths.

4. Conclusions

The creep deformation properties of 7715D titanium alloy and its composite reinforced with TiB and TiC at steady-state stage were mainly investigated in the temperature range from 600 to 700°C. The results can be summarized as follows:

1. Based on the same Widmanstätten $\alpha + \beta$ lath structure, creep resistance of the composite is significantly improved by the addition of TiB and TiC reinforcements in comparison with the matrix alloy.

2. Creep behavior of Class I solid solution is observed for the matrix where viscous dislocation sliding controls the creep behavior. The diagnostic property of the creep deformation curves may be attributed to transition from Class II solution behavior to Class I solution behavior. The apparent stress exponents of the composite are higher than those of the matrix alloy.

(3) Threshold stress can be used to rationally explain the higher stress exponents of the composite. The threshold stresses of the composite obtained at 600°C, 650°C and 700°C are 30 MPa, 18 MPa and 10 MPa, respectively. True stress exponent of the composite is $n = 3.5$.

(4) Except for threshold stress, load transfer and micro-structural strengthening also contribute to the strengthening creep resistance of the composite. The effect of load transfer is very small during the testing range and aggrandizes with increasing temperature. Finer Widmanstätten structures due to addition of the reinforcements contribute to enhancing the creep resistance of the composite.

Acknowledgements

We would like to acknowledge a financial support provided by High Technology Research and Development Program of China under Grant No: 2006AA03Z559, 973 Program under Grant No: 2007CB613806, Program for New Century Excellent Talents in University under Grant No: NCET-07-0549, A Foundation for the Author of National Excellent Doctoral Dissertation of P R China under Grant No: 200332, National Nature Science Foundation of China under Grant No: 50871066 and Research Project of Shanghai Science and Technology Committee under Grant No: 07QB14001.

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