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LC/8YSZ TBCs Thermal Cycling Life and Failure Mechanism under Extreme Temperature Gradients

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Abstract: The purpose of this paper is to study the thermal shock resistance and failure mechanism of La₂Ce₂O₇/8YSZ double-ceramic-layer thermal barrier coatings (LC/8YSZ DCL TBCs) under extreme temperature gradients. At high surface temperatures, thermal shock and infrared temperature measuring modules were used to determine the thermal cycling life and insulation temperature of LC/8YSZ DCL TBCs under extreme temperature gradients by an oxygen-acetylene gas flame testing machine. A viscoelastic model was used to obtain the stress law of solid phase sintering of a coating system using the finite element method. Results and Conclusion: (1) Thermal cycling life was affected by the surface temperature of LC/8YSZ DCL TBCs and decreased sharply with the increase of surface temperature. (2) The LC ceramic surface of the failure coating was sintered, and the higher the temperature, the faster the sintering process. (3) Accelerated life test results showed that high temperature thermal cycling life is not only related to thermal fatigue of ceramic layer, but is also related to the sintering degree of the coating. (4) Although the high temperature thermal stress had great influence on the coating, great sintering stress was produced with sintering of the LC ceramic layer, which is the main cause of LC/8YSZ DCL TBC failure. The above results indicate that for new TBC ceramic materials, especially those for engines above class F, their sinterability should be fully considered. Sintering affects the thermal shock properties at high temperature. Our research results can provide reference for material selection and high temperature performance research.

Keywords: LC/8YSZ DCL TBCs; thermal cycling life; sintering; failure mechanism; finite element analysis

1. Introduction

With the increase of turbine temperatures of aero engines and gas turbines, the problem of high-temperature sintering of thermal barrier coatings becomes more and more serious [1,2]. When the turbine temperature exceeds 1200 °C, APS coatings will sinter quickly, resulting in coating densification and thermodynamic performance degradation [3–5]. At present, the sintering of APS coatings mainly focuses on the evolution of thermodynamic parameters of coatings with sintering time [6–10]. Based on experimental observations of microstructure evolution of APS coatings during sintering [11–13], Siebert et al. found that the formation of an interlaminar sintered neck would increase the Young's modulus of the coating, and no phase change would occur in this process [14–16]. The experiments of Hardwicke et al. showed that the formation of a sintered neck strengthened the heat transfer between plates and thus increased the thermal conductivity of the coating [17–19].

Cipitria et al. established a sintering model based on microstructures by using the variational principle, in which the elastic model was adopted to predict the microstructure and thermal conductivity evolution of the coating, but ignored the creep behavior of the coating at high temperature [20–24]. Kumar and Cocks developed constitutive models



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). involving elasticity, local contact, sintering, diffusion, and creep behavior. On this basis, they further proposed a brick model to describe the microstructure evolution of coating sintering and predicted the influence of coating response and crack density on thermal conductivity under high temperature compression. Although this model systematically investigated the key factors in the process of coating high-temperature sintering, it simplified the sintered neck into mechanical connection, making it difficult to research the force and thermal behavior of the sintered neck [25–27]. Lv [9,28,29] found that there are often angles between lamella, presenting a wedge structure, which is not a traditional brick assumption in the model of parallel plate layer structures by an APS coating layer table interface topography evolution of experimental observation. To this end, they established an APS coating microstructure model and wedge model considering a sintering neck and adopted an improved elasto-viscoplastic thermodynamic coupling constitutive model to discuss the influence of sintering neck formation on coating force and thermal behavior. Our team's research [12] found that sintering was the main cause of LC layer peeling-off of LC/8YSZ DLC TBCs by 1250 °C thermal shock experiments, where a longitudinal crack is formed first in the sintering process, and horizontal cracks form and expand at the longitudinal crack tip.

At present, the sintering mechanism of APS coatings has only been preliminarily discussed, and the influence of sintering on the thermal shock resistance of coatings in the process of high-temperature thermal shock is rarely studied. LC can retain phase stability (cubic fluorite structure) as well as lower thermal conductivity (about 0.7 W·m⁻¹·K⁻¹ at 1200 °C) after long-term annealing at 1400 °C. In addition, LC has a larger thermal expansion coefficient than 8YSZ due to its disordered fluorite structure with 1/8 sites as oxygen vacancies [12]. Therefore, LC is one of the candidate materials for thermal barrier coatings. In this paper, based on the optimization results of layer thickness ratio of double-layer thermal barrier coatings in the early stage, LC/8YSZ DLC TBCs, with a thickness ratio of the LC and YSZ layer of 1:1, was selected as the research object to analyze sintering behavior in the process of high-temperature thermal impact. Through finite element simulation, the influence of temperature, porosity, and other factors on high-temperature sintering is explored.

2. Materials and Experimental Section

2.1. Materials and TBCs Preparation

LC/8YSZ DCL TBCs thermal barrier coatings, composed of an alloy bonding layer and two ceramic coating layers, were deposited by high efficiency supersonic atmospheric plasma spraying (SAPS, Xi'an Jiaotong University, Xi'an, China) on a Ni-based superalloy. Commercial CoNiCrAIY powder (AMDRY 4454, Sulzer Metco, New York, NY, USA) was used as the spraying material for the alloy bonding layer. In this experiment, yttrium partially stable zirconia and lanthanum cerate (La₂Ce₂O₇, LC) were selected as the original powders to prepare an intermediate ceramic layer and a top ceramic layer, respectively. The surface morphology of YSZ powder and LC powder are shown in Figures 1 and 2. Commercial 8 wt % yttrium stabilized zirconia (8YSZ) powder (SY-133, Sangrao Technology Co., LTD., Beijing, China) is an agglomerated spherical particle with a size of 15–45 μ m. The LC ceramic layer is made of spray dried spindled LC (LC001, Beijing Jinlunkuntian Special Machine co., LTD., Beijing, China) with a particle size of 45–106 μ m.

The Ni-based superalloy is GH4169 with a diameter of 30 mm and a thickness of 6 mm. Before spraying, the superalloy matrix was placed in acetone for ultrasonic treatment to remove the grease on the surface. After decontamination, suction sandblasting equipment (gas pressure was 0.8 MPa, size of brown corundum sand and gravel was 40–80 mesh) was used to sandblast the matrix. SAPS was used to prepare an 80 μ m bonding layer, a 110 μ m YSZ layer, and a 110 μ m LC layer, respectively, on the surface of the preheated 150 °C superalloy matrix.

Figure 3 depicts the cross-sectional morphology of the as-sprayed LC/8YSZ coating. As shown in Figure 3, the LC and YSZ layer well connected with each other. There were fewer large pores in the LC layer and more pores in the YSZ layer.



Figure 1. Morphology of YSZ powder.



Figure 2. Morphology of LC powder.



Figure 3. Cross-sectional morphology of as-sprayed LC/8YSZ coating.

2.2. Thermal Cycling Performance and Thermo-Physical Performance Test

The TBC was heated to the target temperature by a C_3H_8 flame burner (Xi'an Shuntai Thermal Mechanical and Electrical Equipment co., LTD., Xi'an, China) ($C_3H_8:O_2 = 3200 \pm 50 \text{ mL} \cdot \text{min}^{-1}/2800 \pm 50 \text{ mL} \cdot \text{min}^{-1}$) and held for 5 min, then cooled to room temperature with compressed air within 40 s to test the thermal cycling performance of the coating. During heating, the back of the superalloy sample was cooled with 40 mL/min of compressed air to maintain a temperature gradient in the direction of coating thickness. Once

heating and cooling were regarded as one thermal cycling, and the thermal cycling life was the number of thermalcycling when the coating surface was peeled off by 10%. To test the temperature gradient in the direction of coating thickness, the surface and back temperatures of the coating were monitored by Raytek MI3 1M and 2M (MI3, Raytek, Santa Cruz, SC, USA) with reflectance spectra of 1 μ m and 1.6 μ m, respectively.

Accelerated life test is an important reliability test, which is a method to test, analyze, and evaluate the reliability of products. There are more and more thermal barrier coatings with high reliability and long life with the rapid improvement of high temperature performance. A life test under normal stress and temperature to evaluate its reliability cannot meet the actual needs, and the cost is very high. An accelerated life test is carried out by increasing the stress level factor in order to shorten the test time without changing the failure mode. In this paper, the stress level factor was the thermal cycling temperature, and the thermal cycling times of 1350 °C and 1450 °C were tested, respectively. Twelve samples were tested for each stress level. The acceleration life equation was obtained by the acceleration life module of Minitab software (Minitab 20, Pennsylvania State University, State College, PA, USA). Thermal conductivity, thermal diffusivity, and specific heat capacity were measured using a laser thermal conductivity meter (LFA 457 MicroFlas, NETZSCH Scientific Instrument Trading (Shanghai) Co., LTD., Shanghai, China). The test ceramic coatings were obtained by spraying a 1 mm thick coating on a φ 12.7 mm aluminum substrate and then etching off the aluminum with hydrochloric acid.

2.3. Simulation of Coating Sintering Process

The constitutive model is the core of sintering simulations of thermal barrier coating ceramic layers. ABAQUS CREEP provides an interface for a user-defined constitutive model. In this paper, the viscoelastic constitutive model [30–33] was programmed as CREEP user a subroutine in which the sintered CREEP part was expressed as the CREEP strain increment, including the CREEP component and the volume expansion component:

$$\Delta \varepsilon^{cr} = \frac{1}{3} \Delta \overline{\varepsilon}^{ve} R + \Delta \overline{\varepsilon}^{cr} n \tag{1}$$

where $\Delta \overline{\epsilon}^{ve}$ is the increment of volumetric expansion strain, $\Delta \overline{\epsilon}^{cr}$ is the equivalent creep strain increment, n is the gradient of the stress partial component potential.

The creep strain rate follows the linear law of viscosity and is similar to the viscoelastic constitutive model. Therefore, the creep strain rate can be expressed as

$$\dot{\varepsilon}^{cr} = \frac{\sigma_o}{2n_s} + I \frac{\sigma_m - \sigma_s}{3n_b} \tag{2}$$

where $\frac{\sigma_o}{2n_s}$ means change in shape, and $I\frac{\sigma_m - \sigma_s}{3n_b}$ means change in volume, respectively. σ_o is the stress bias tensor, σ_m is the isostatic pressure, I is unit tensor, n_s is the shear viscosity, n_b is the volume viscosity, and σ_s is the sintering stress, respectively.

According to Equation (2), the creep strain increment is

$$\Delta \varepsilon^{cr} = \frac{tr(\sigma)\Delta t - 3\sigma_s \Delta t}{9n_s}I + \frac{\sigma_o \Delta t}{2n_b}$$
(3)

By comparing Equations (1) and (3), the increment of volumetric expansion strain and equivalent creep strain can be obtained as follows:

$$\Delta \bar{\varepsilon}^{ve} = \frac{tr(\sigma) - 3\sigma_s}{3n_s} \Delta t \tag{4}$$

$$\Delta \bar{\varepsilon}^{cr} = \frac{\bar{q} \Delta t}{3n_b} \tag{5}$$

where $p = -\frac{tr(\sigma)}{3}$ is the equivalent compressive stress, \tilde{q} is the equivalent stress partial component.

To study the sintering behavior of the coating, the following simulation conditions were established: two-dimensional cylindrical cross-section samples of the same size as the experimental samples were used. The interlayer interfaces of LC/8YSZ and 8YSZ/BC were semicircular curved undulating interfaces with a radius of 5 µm. The TBCs sample was subjected to gravity during simulated sintering. A thermal load was applied on the surface of the sample at an initial temperature of 20 °C. In each incremental step of time, the temperature was transferred to other parts of the sample through heat conduction at a heating rate of 20 °C/min. The LC layer surface of the sample was heated from 20 °C to the target temperature for 4 h, and then cooled to room temperature. In this study, a twodimensional axisymmetric model was adopted, which is the same as in reference [12]. The left and bottom sides of the two-dimensional model were constrained, and the symmetrical boundary condition adopted for the left Y-axis was U1 = UR2 = UR3 = 0 (U1: translational degrees of freedom along the X-axis; UR2: rotational degrees of freedom along the Y axis; UR3: rotational degrees of freedom along the Z-axis). The symmetric boundary condition adopted for the bottom X-axis was U2 = UR1 = UR3 = 0 (U2: translational degrees of freedom along the Y-axis; UR1: rotational degrees of freedom along the X-axis).

3. Results and Discussion

3.1. Thermal Shock Resistance via Accelerated Life Test

In order to study the thermal shock resistance of TBCs at high temperatures, LC/8YSZ DCL TBC samples for different surface temperatures were tested to determine their thermal cycling life. Digital photo surface morphology of the thermal barrier coating under different times at 1350 °C and 1450 °C thermal cycling are shown in Figures 4 and 5, respectively. As can be seen from Figure 4, tiny spot-like spalling was formed at the edge of the sample at first, and then the spalling area gradually expanded. After a certain number of cycles, the middle area of the sample began to spall and gradually expanded until the coating failed. Figure 5 shows that the sample also started with spot-like spalling at the edge, and then large areas of spalling occurred after a certain number of cycles.



Figure 4. Surface morphology of LC/8YSZ DCL TBCs after different thermal cycling at 1350 °C.



Figure 5. Surface morphology of LC/8YSZ DCL TBCs after different thermal cycling at 1450 °C.

The surface of the failure coating appeared as a fish-scale structure, which is an undulating surface caused by flaking (Figure 6a,c). As seen in Figure 6b, the columnar crystal was rounder and smoother than that of the original TBCs, which is the result of columnar crystal fusion caused by coating sintering. However, in Figure 6d, the columnar crystal structure can no longer be observed, and grains are fused, making it impossible to distinguish the columnar crystal and equiaxed crystal structures within the coating. Moreover, due to serious sintering, the pore size of the coating gradually decreased. Energy dispersive spectrometer (EDS) results (Figure 6e,f) showed that spalling occurred within the LC layer at 1350 °C thermal cycling and at the LC/8YSZ interface at 1450 °C thermal cycling. To explore the spalling position of the coating, the elements on the spalling surface were tested (Figure 6e,f). Figure 6e shows that the main elements of the surface include La, Ce, and O, indicating that the sample spalling occurred within the LC layer (At 1350 °C thermal cycling). Figure 6f shows that Zr and O elements were detected (at 1450 °C thermal cycling). This suggests that the LC layer of the LC/YSZ DCL TBCs was completely peeled off. This is also consistent with the results of section morphology (Figure 7).



Figure 6. (**a**,**b**,**e**) The SEM surface morphology and EDS result of LC/8YSZ DCL TBCs after failure at 1350 °C thermal cycling; (**c**,**d**,**f**) the SEM surface morphology and EDS results of LC/8YSZ DCL TBCs after failure at 1450 °C thermal cycling.



Figure 7. Cross-sectional morphology after failure at 1350 °C (a,b) and 1450 °C (c,d).

3.2. Accelerated Life Test and Life Prediction

Under different thermal shock temperatures (1350 °C and 1450 °C), the two-parameter Weibull distribution curve of TBCs is shown in Figure 8; the ordinate is the failure probability of TBCs, and the abaxial is the number of thermal cycling. In Figure 8, β represents the slope of the fitting curve. Transverse curves N10, N50, and N90 represent the TBC thermal cycling number at a failure probability of 10%, 50%, and 90% (Table 1). It should be noted that the Weibull distribution curve presents an obvious dual-zone model when the thermal shock temperature is 1350 °C. The slope of the Weibull life distribution curve is disparate in these two intervals. The existence of this dual-zone model not only means that the thermal cycling life of the TBCs has high dispersion, but also indicates that the failure mode and mechanism of the thermal barrier coating are obviously different under this temperature condition.



Figure 8. Weibull distribution of thermal cycling life.

Thermal Cycling Temperature (°C)	Failure Probability	Thermal Cycling Number	Standard Error	95% Normal Confidence Interval	
				Lower Limits	Upper Limits
1350	N10	37.7	3.7	31.2	45.7
	N50	51.4	2.5	46.7	56.6
	N90	62.7	2.7	57.6	68.2
1450	N10	6.7	0.5	5.7	7.8
	N50	7.9	0.5	6.9	9.2
	N90	8.9	0.6	7.8	10.3
Forecast Result					
1250	N10	348.6	40.5	277.7	437.8
	N50	442.3	47.7	357.9	546.4
	N90	514.6	58.9	411.3	643.9

Table 1. Fitting values at various temperatures.

The slope of the Weibull distribution curve can generally be used to characterize the dispersion degree of thermal cycling life. A larger slope value indicates that the dispersion degree of the thermal cycling life is lower, and the thermal shock parameters of the coating are easy to predict. On the contrary, when the thermal cycling life of the coating is more dispersed, the thermal shock parameters have greater dispersion. Table 1 shows the life parameters of the coating at different thermal shock temperatures. It is clear that the life parameters of the TBCs decrease with increases in temperature. At low temperature, the slope value of the Weibull distribution curve is relatively small, indicating that the dispersion degree of contact fatigue life of the thermal barrier coating is relatively high.

Generally speaking, the thermal cycling life of TBCs is short in the water-cooling mode, and the Al has not been exhausted in the bonding layer and the interface cracking of the ceramic layer/bonding layer has not been caused. Therefore, the failure mode of thermal barrier coating is mainly the ceramic layer spalling caused by thermal fatigue in the process of thermal shock. However, a precondition is that the thermal shock temperature is low enough to fail to sinter the ceramic layer. Once the thermal shock temperature is high enough for the coating to be sintered, the coating failure caused by sintering needs to be considered. Some studies have shown that LC bulk materials are not easy to sinter below 1400 °C. However, as shown in Figure 6, columnar grains are sintered in the LC layer at a thermal shock temperature of 1350 °C. The root cause of this phenomenon is related to the tiny spot-like spalling of the LC layer. The surface of the LC layer is convex and concave after tiny spot-like spalling occurs in the process of thermal shock. Under the same high-temperature flame flow, the convex points on the surface are heated above the sintering temperature, where the coating is sintered and the porosity is reduced. Sintering also accelerates the spalling of the coating and the failure rate of the coating. Therefore, in the process of high-temperature thermal shock, the failure of the coating is the result of the combined action of thermal fatigue and sintering, which is also consistent with the Weibull two-interval model.

Calculated according to the data in Table 1, the intercept of the mathematical model for the number of cycles is -28.3442, the heating temperature coefficient is 4.58588, and the shape parameter is 7.92128. Thus, the mathematical model for the accelerated life experiment can be obtained:

$$N_f = 4.58588T_1 + \frac{1}{7.92128}\epsilon_p - 28.3442 \tag{6}$$

where N_f is the thermal cycling number, T_1 is the thermal shock temperature, and ϵ_p is the percentile value of *Pth*.

Figure 9 show the variation trend of various life parameters of TBCs with thermal shock temperature. The T–N curve and function equation of the coating can be obtained

by fitting. Through this mathematical model, we can predict the number of cycles of the coating at different temperatures.



Figure 9. Predicted thermal cycling life at different temperatures.

As shown in Figure 9, the thermal cycle life of the coating under three failure probabilities can be obtained intuitively by means of T–N curves at any thermal shock temperature. Of course, in the T–N curve, P can be any value in the range of 0–100% by calculation of Weibull distribution function, and is not limited to 10%, 50%, and 90% by any means. Here, three typical failure probabilities were selected to describe the T–N curve. Through the establishment of T–N curves under different failure probabilities, the thermal cycle life of parts of the surface under any thermal shock temperature and any failure probability can be obtained, and the life prediction of thermal barrier coating can be completed.

3.3. Heat Insulation Capability of LC/8YSZ DCL TBCs

Figure 10a–c shows the thermal physical property parameters (thermal conductivity, thermal diffusion coefficient, and specific heat capacity) of LC, YSZ, and LC/YSZ coatings. The thermal diffusion coefficient and specific heat capacity of two single ceramic layer coatings have the same change rule. With the increase of temperature, the thermal diffusion coefficient decreases, but the specific heat capacity increases. However, the thermal conductivity of them is opposite. The thermal conductivity of LC coating increases with the increase of temperature and decreases slightly at 400 °C. The thermal conductivity of YSZ layer decreases, and the inflection point occurs at 800 °C.



Figure 10. Thermal physical property parameters of LC (**a**), YSZ (**b**), and LC/8YSZ (**c**) coatings from 200 °C to 1200 °C.

According to the relationship between the thermal physical property parameters,

λ

$$=\rho\alpha c \tag{7}$$

where λ is thermal conductivity, ρ is density, α is thermal diffusion, and *c* is specific heat capacity. According to Equation (7), the thermal conductivity value of LC/YSZ DCL TBCs should be between the thermal conductivity value of LC and YSZ. This result is consistent with Figure 10. The thermal conductivity of LC/YSZ coating decreases with increasing temperature and increases slightly at 400 °C. The above thermal physical property parameters were used in the following ABAQUS finite element simulation.

3.4. Finite Element Simulation of Relative Density and Stress of DCL TBCs

Figures 11 and 12 are the relative density curve of the LC layer. By comparing Figures 11 and 12, we find that grain size has a great influence on the relative density. When the LC grain size is 30 nm, the relative density decreases from 0.82 to about 0.79 before the creep temperature is reached. After the creep temperature is reached, the relative density increases rapidly and exceeds 0.95. Finally, as the temperature gradually decreases to room temperature, the relative density continues to increase to 1. For LC coatings with micron grains, the relative density drops to between 0.77 and 0.78 before reaching the creep temperature. When the temperature reaches the creep temperature, the relative density increases by 0.01. In the cooling stage, the relative density increases rapidly and finally reaches or approaches 0.83.

In the sintering process, the relative density of LC layer generally decreases first and then increases. Before creep (the heating stage), the relative density decreases due to the thermal expansion of LC layer. When the temperature is higher than the creep temperature (the heat preservation stage), the creep mechanism plays a major role, resulting in the relative density increase of the material. In the cooling stage, the relative density of LC layer increases slightly, which is caused by the cooling shrinkage. Grain size affects the sintering property of material. Nanocrystalline size material has high activity, short atomic diffusion distance, and fast transfer mechanisms. During the creep stage, relative density of material increases noticeably. In contrast, the relative density of micron grain size material increases very little during the creep stage.



Figure 11. Relative density curve of LC with nano grain.



Figure 12. Relative density curve of LC with micron grain.

Figure 13 shows the variation of the distance between the main stress and the surface in the coating after the wave peak. It can be seen from Figure 13 that the principal stress of LC/8YSZ and 8YSZ/BC peaks is tensile stress, which increases with the sintering temperature increase. For the nano-coating, the tensile stress of 8YSZ/BC peak (51–97 MPa) is greater than that of LC/8YSZ peak (32–58 MPa), and the stress increases by 19–39 MPa. The stress range of the micron coating peak is very small, but the stress of the 8YSZ/BC peak is 55 MPa larger than that of the LC/8YSZ peak. Figure 14 shows the variation of the linear principal stress distance between the surface and the trough in the coating. The maximum principal stress of the 8YSZ/BC trough is compressive stress, and the stress value increases with the temperature increase for both nano- and micron-coatings. The maximum principal stress of the LC/8YSZ wave trough of the micron coating is compressive stress, while that of the nano-coating is tensile stress, and the stress value also increases with the temperature increase.



Figure 13. Maximum principal stress of the wave peak.



Figure 14. Maximum principal stress of the trough.

4. Conclusions

In this paper, a series of accelerated life tests were designed to study the thermal shock resistance of LC/8YSZ DCL TBCs at high temperature and analyze the failure mechanism of TBCs. Our experimental results show that the high temperature of 1350 °C or above leads to the sintering of the coating during the thermal shock process, and the thermal fatigue and sintering of the ceramic layer together affect the thermal cycling life. The thermal shock resistance decreases sharply with the increase of temperature. Considering the sintering creep as creep strain increment, it is concluded that the sintering of the LC layer produces a large sintering stress, which is one of the main reasons for the coating failure. The above results indicate that the design of the anti-sintering structure should be taken into full consideration in the structural design of TBCs for ultra-high temperature. In general, there are relatively few systematic studies on the sintering of TBCs during thermal impact, and the experimental methods are limited and primitive. In order to further explore the effect of sintering on thermal impact of thermal barrier coatings, it is necessary to develop in situ high temperature measurement methods and devices for real-time characterization of the dynamic evolution of microstructures and properties during thermal shock tests in future research.

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