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Construction of the master sintering curve for submicron size α-Al_2O_3 based on non-isothermal sintering containing lower heating rates only

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The master sintering curve (MSC) is quite useful for analyzing the shrinkage behaviour of ceramics. In this study, the shrinkage behaviour for α-Al_2O_3 with a mean particle size of 350 nm during constant-heating-rate sintering were evaluated based on the MSC theory. An MSC for the above powder has been constructed using dilatometry data containing heating rates lower than 5 °C/min only with the help of combined-stage sintering model. The validity of the MSC has been verified by a few experimental runs. A comparison between predicted and experimental shrinkage curves showed good consistency, thus confirming that it is possible to control shrinkage behaviour using the MSC. The concept of the MSC has been used to evaluate the apparent activation energy for the above powder, and a high value of 1035 kJ/mol was obtained.

Key words: *low heating rate; master sintering curve; apparent activation energy; α-Al_2O_3*

1. Introduction

Sintering is a crucial step in the fabrication of α-Al_2O_3 ceramic components from a powder compact and involves microstructure evolution through the action of several different mechanisms [1]. Analysis of densification during non-isothermal sintering with constant heating rates allows one to follow more closely microstructure evolution.

Since the 1940s, many researchers have proposed sintering theories that have been verified by experimental examinations [2, 3]. These theories are, however, limited to a single transportation process and a single stage. Such theories are insufficient for evaluating sintering behaviours. Hansen et al. [4] proposed a generalized model with a sintering equation for the shrinkage rate, quantifying sintering as a continuous process from the beginning to the end. The microstructure is characterized by two separate parameters representing the geometry and scale (average grain size). Based on the generalized model, Su and Johnson [5] extended a classic sintering theory and proposed the master sintering curve (MSC).

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The MSC is empirically derived from densification data obtained over a range of heating rates [6]. When a proper activation energy is used, all the data converge onto a single curve, the MSC. The activation energy can be readily estimated with just a few dilatometer experiments if it is unknown beforehand. Once established, the MSC makes it possible to predict the final density after arbitrary temperature-time excursions. It is particularly useful when considering alternative sintering methods [7]. This curve is sensitive to such factors as the starting morphology of the powder, fabrication route, dominant diffusion mechanism and heating condition used for sintering. Thus the MSC curve can also be used as an aid to compare the sinterability of various powders [8–10] and to know the effects of additives, atmosphere and fabrication procedure of sintering [6]. In the MSC theory, $\Phi(\rho)$ which is function only of density, is given as the function of temperature and time:

$$\Phi(\rho)=\Theta(t,T(t))=\int_0^t \frac{1}{T}\exp\left(-\frac{Q}{RT}\right)dt \tag{1}$$

where Q is the apparent activation energy for sintering, R – the gas constant, T – the absolute temperature, t – the time. In this case, if one dominant diffusion mechanism exists and the microstructure is a function only of density, a unique MSC can be obtained dependent on the powder and green body characteristics, which are independent of the heating profile.

The relationship between the density ρ and Θ is defined as the master sintering curve. For the construction of MSC, a series of runs at constant heating rates over a range of heating rates is needed. In the past, the heating rate used for the construction of the MSC for α-Al_2O_3 inevitably contains higher values (higher than the heating rate of 5 °C/min) [6, 11, 12], little attention was paid to the sintering process containing heating rates lower than 5 °C/min only.

It is well known that surface diffusion inhibits sintering, particularly at low temperatures and during the earliest stages of sintering. In constant heating rate sintering, this inhibition diminishes with time and increased temperature. Estimates of the activation energy of densification are biased upward by this surface diffusion effect, particularly at low heating rates. The MSC for low heating rates in the presence of low activation energy surface diffusion would be biased to higher temperatures from those at higher heating rates.

In ceramic powder processing, high heating rates are often used to enhance sintering and reduce grain growth. The essence of this concept is that fast heating rates favour densification instead of grain growth in coarsening sensitive systems (i.e., with higher activation energy for densification than for grain growth). In these systems, a slow heating rate results in grain coarsening by surface diffusion which is able to operate through low temperature ranges. Conversely, a high heating rate takes the system to high temperatures where a high densification rate is favoured before surface diffusion causes grain growth. Moreover, a slower heating rate produced a higher densification of samples because time available for densification in this case was longer.

The objectives of this study were to construct the MSC for α-Al_2O_3 based on non-isothermal sintering containing lower heating rates only, to determine whether the MSC can be applied to predict and control the α-Al_2O_3 sintering, and to apply the MSC to determine the sintering activation energy.

2. Experimental

For constant-heating-rate sintering, α-Al_2O_3 powder (99.9% purity, Dalian Luming Nanometer Material Ltd, Dalian, China) having an average particle size of 350 nm was mixed with 1 wt. % adhesion agent, dried, granulated, and screened to –60 mesh. The powder was pressed using a uniaxial pressure of 80 MPa and then further consolidated by cold isostatic pressing at 250 MPa to create bars of ca. 5×5×45 mm^3. The binder was burned out at 500 °C. This resulted in negligible densification but provided green strength and minimized contamination from any adsorbed species in the raw powder. The green density was measured by the geometric method. The green density of α-Al_2O_3 powder compacts was 2.08±0.03 g/cm^3. The value of 3.98 g/cm^3 was used as the theoretical density (ρ_0), which was the single crystal density.

The shrinkage of α-Al_2O_3 samples was measured with a push rod type dilatometer in the axial direction. The length change measurements were made with a linear voltage differential transducer (LVDT) which was maintained at a constant temperature by means of water circulation from a constant temperature bath. The accuracy of the measurement of the change in length was within ±0.1 μm. The temperature was measured using a calibrated thermocouple placed directly above the sample. A small force of 0.2 N was applied to the sample through the push rod.

First, two green compacts were heated to the peak temperature (the temperature corresponding to the end of the sintering) at the heating rate of 2 and 5 °C/min. Secondly, three green compacts were sintered by heating up to 1200, 1350 and 1500 °C with holding time for 6 h at the heating rate of 5 °C/min. Finally, other runs for non-isothermal sintering were carried out in the same system by heating at 1 °C/min to 1115 °C, 2 °C/min to 1250 °C, 3 °C/min to 1420 °C, 4 °C/min to 1575 °C and 5°C/min to 1650 °C without holding dwell time, respectively. Apparent densities of the sintered samples were determined by the Archimedes method.

3. Results and discussion

3.1. Construction of the master sintering curve

Figure 1 shows temperature dependence of the $\Delta L/L_0$ of α-Al_2O_3 under two heating rates. The dilatometric curves of Fig. 1 were replotted as the relative density ver-

sus temperature (Fig. 2). The $\Delta L/L_0$ (shrinkage) values were converted into the time-dependent relative density ρ using the following dependence [13]:

$$\rho = \frac{\rho_G}{\left(1-\frac{\Delta L}{L_0}\right)^3}\frac{1}{\rho_0} \tag{2}$$

where ρ_G is the density of the green compact, ρ_0 is the theoretical density. The curves have the familiar sigmoidal shape and generally shifted to higher temperatures with increasing heating rate.

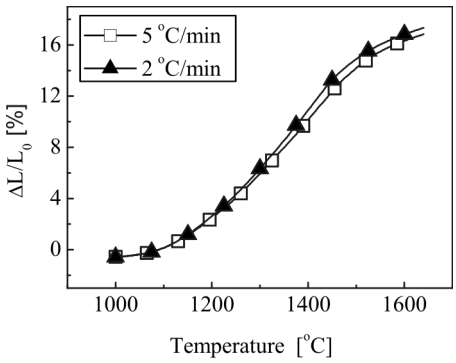

Fig. 1. Sintering curves for α-Al_2O_3 powder compacts at two heating rates

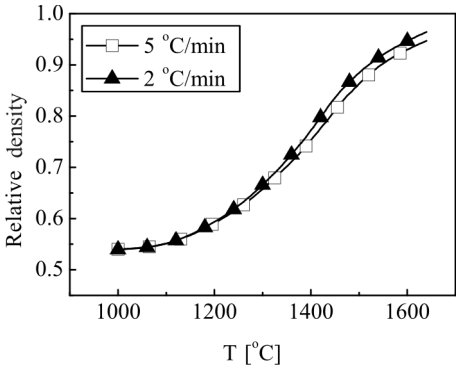

Fig. 2. Relative density in function of sintering temperature

For the construction of MSC, the integral of Eq. (1) and the experimental density should be known. The dilatometry can be conveniently used to determine the density since the instantaneous density at all times can be obtained from the dilatometric data [14]. For the calculation of Θ, the activation energy (a characteristic quantity that elucidates the fundamental diffusion mechanisms during the sintering process) should be

known. If the activation energy is unknown, it can be estimated with a good precision from Θ vs. density ρ data [6, 15].

For this purpose, initially, an estimate is made for the activation energy Q, and the MSCs for all the heating profiles are computed using Eq. (1). If the correct value of Q has been given, all the data converge to a single curve. A curve (a polynomial function) can be fitted to all the data points, and then the convergence of the data to the fitted line can be quantified through the sum of the residual squares of the points with respect to the fitted line. Another estimate of Q is made, and the process is repeated (Fig. 3a–d). When the best estimate of Q is found, the mean of residual (sum of residual squares divided by total number of data points) is a minimum.

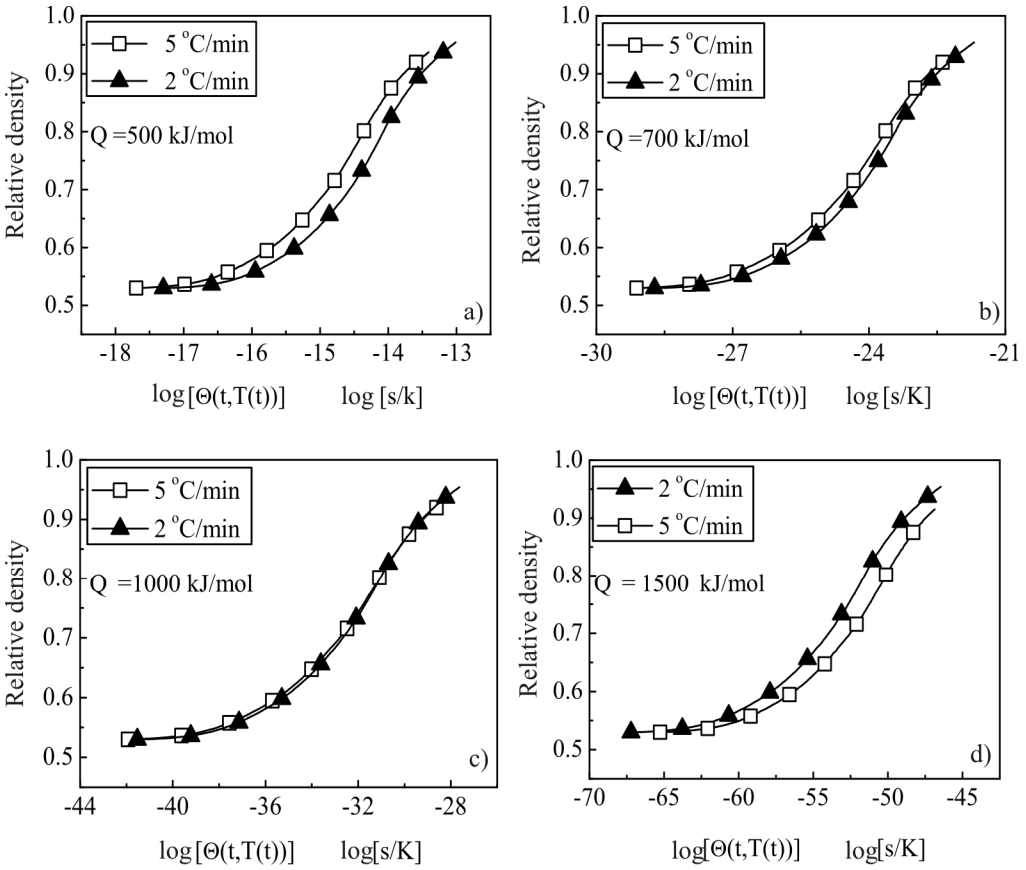

Fig. 3. Construction of a ρ–Θ curve for various heating profiles for a chosen value of activation energy: a) 500 kJ/mol, b) 700 kJ/mol, c) 1000 kJ/mol, d) 1500kJ/mol

The results for such an exercise for the alumina sintering data of Fig. 2 are shown in Fig. 4.The minimum is reached at ca. 1035 kJ/mol, indicating the estimated sintering activation energy. It is a high estimate, considering the reported activation energies for alumina in the literature [11, 12].

The activation energy of α-Al_2O_3 obtained by Tatami et al. [11] for heating rates 7.5–20 °C/min was 555 kJ/mol based on the MSC theory. In their experiments, the powder was uniaxially molded at 50 MPa, followed by cold isostatic pressing at 200 MPa. Shrinkage behaviour during sintering of the green bodies was evaluated using an electric furnace equipped with a dilatometer. The samples were heated to 1400 °C at constant heating rates (7.5, 10, 15, 20 °C/min). The shrinkage ranging from 2.5 to 17.5% was analyzed. It was found that the MSCs obtained by sintering at the heating rate of 3–5 °C/min did not correspond to that based on the heating rate of 7.5–20 °C/min [11]. It can be presumed that contribution of the surface diffusion for the slow heating rate becomes large. For this reason, in firing at 3–5 °C/min, densification proceeded by a diffusion mechanism different from the others. In other words, the activation energy at 3–5 °C/min sintering differed from that at 7.5–20 °C/min firing.

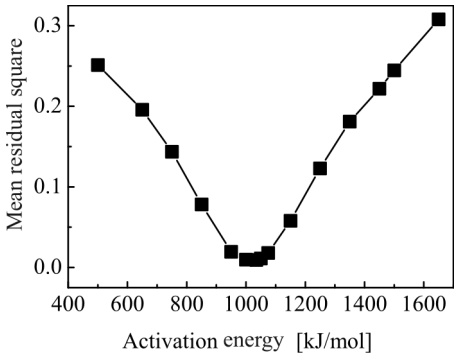

Fig. 4. Dependence of mean of residual squares on the activation energy; minimum at 1035 kJ/mol

In the α-alumina (with the average particle size of 0.27 μm) sintering experiments by Wang and Raj [12], the activation energy was determined to be 440 kJ/mol from an Arrhenius plot of $\ln(\dot{\varepsilon}T)$ vs. the reciprocal of the absolute temperature. Five values of density ranging from 0.65 to 0.85 are used. The cylindrical samples themselves were prepared by uniaxial pressing in a steel die at 40 MPa and then by isopressing cylindrical green compacts at 100 MPa. The samples were 12 mm in diameter and 10 mm high. Their relative green density was 55±1%. The temperature of the specimen was raised to 800 °C in 1 h and held at that temperature for 10 min. Thereafter three different heating rates (5, 10, and 20 °C/min) were used to increase the temperature from 800 °C to 1600 °C. The experiments were terminated when the temperature reached 1600 °C.

In the ZnO sintering experiments by Chu et al. [5], all the powder compacts were heated first to 500 °C at 10 °C/min and then heated to 1100 °C at a wide range of heating rates (0.5, 2, 5, 10 and 15 °C/min). Closer inspection of the MSCs derived from the experimental data showed that the points calculated from the data of the lowest heating rate (0.5 °C/min) experiment were a little lower than those from higher heating rate

experiments. i.e., using 0.5–15 °C/min, yields an apparent activation energy of 310 kJ/mol. Excluding the lowest and the two lowest heating rate data from the analysis results in estimates of 300 and 285 kJ/mol, respectively. This could be ascribed to a surface diffusion effect, which would have a more significant effect at lower heating rates.

It should be noted that the activation energy value obtained in the present work is quite high (almost twice as high as 555 kJ/mol obtained by Tatami et al. [11] for heating rates 7.5–20 °C/min or Wang and Raj [12] of 440 kJ/mol) and differs much more significantly than that in the discussed case of ZnO.

During sintering, surface transport mechanisms (evaporation condensation, E-C; surface diffusion, SD) provide for neck growth by moving mass from surface sources. Bulk transport processes (grain boundary diffusion, GB; volume diffusion, VD; plastic flow, PF) provide for neck growth using internal mass sources. Only bulk transport mechanisms cause shrinkage. However, a major complication arises due to multiple mechanisms contributing simultaneously to shrinkage. The activation energy for sintering is equal to the activation energy for the rate-controlling diffusional mechanism since the sintering rate is proportional to the diffusion coefficient. However, the value obtained for Q can vary drastically, depending on the conditions (i.e., the characteristics of the raw materials, the preparation procedure of green compacts, the sintering procedure, etc.) under which the sintering data are obtained.

As has been shown, the condition under which the activation energy was obtained in the literature [5, 11, 12] differs significantly from that in the present work, especially the heating rate (heating rates lower than 5 °C/min only employed in the present work). According to the sintering theory, the activation energy of sintering should be consistent with that of the apparent diffusion coefficient of the rate-limiting species of sintering. In sintering polycrystalline ceramics, it is common that both grain boundary and lattice diffusion of the rate-limiting species can simultaneously contribute to densification. Some reports [16, 17] have suggested that the change of the relative contribution of D_l and D_b (D_l is the lattice diffusion and D_b is the grain boundary diffusion) due to the difference of the impurity level or grain size can affect not only the pre-exponential factor but also the activation energy of the apparent diffusion coefficient. However, the relative contribution of D_l and D_b also is different at different temperatures even impurity level and grain size are the same because these two diffusivities have different temperature-dependences. Thus, heating rate would have a significant influence on the non-isothermal kinetic processes due to the fact that it can change the relative contribution of D_l and D_b from low to high temperatures. Therefore, the higher activation energies evaluated based on the non-isothermal sintering can be attributed to the effect of heating rate [18]. Especially for the small-grain-size powder, due to the fact that its densification can occur at lower temperatures. Thus, the contribution of D_b to densification will be higher because of the higher degree of densification in the lower temperatures using lower heating rates, which in turn would influence the evaluation of the activation energy.

Moreover, German [19] pointed out that diffusivities could vary widely with impurity content and atmosphere. In the present work, the increase in carbon content is due to the binder residue left behind after the debinding process. Thus, the presence of binder residue and impurities on the particle surfaces after the binder has decomposed may also be a cause leading to the higher activation energies found in the present research.

It is obvious that in the present work the samples have not achieved full density (about 96% of the theoretic density) and that the activation energy value is similar to the one obtained by Fang et al. [18] (1080 kJ/mol) for classified α-Al_2O_3 compacts in the intermediate stage of sintering.

In the literature [18], the classified powder had an average diameter of 0.21 μm. Sintering was performed in air using a dilatometer. For nonisothermal sintering, four heating rates of 3, 5, 10, and 20 °C/min were used to reach the desired temperature (1700 °C) without holding. The activation energy of sintering could essentially be evaluated from the Arrhenius plot of $\ln(\dot{\varepsilon}T)$ vs. the reciprocal of the absolute temperature. Five values of density ranging from 0.70 to 0.90 were used.

For the classified powder, three values of activation energy in the intermediate stage of sintering can be evaluated based on different heating rates, i.e., 478 kJ/mol for 10 and 20 °C/min, 640 kJ/mol for 5, 10, and 20 °C/min, and 1080 kJ/mol for 3, 5, and 10 °C/min, respectively. It indicated that a higher value of the evaluated activation energy will be obtained when the Arrhenius plot involves low heating rates, which further supports that the relative contribution of D_l and D_b to densification is different at the same density level for high and low heating rates. Comparing the activation energy of 1080 kJ/mol in the literature and 1035 kJ/mol obtained in the present work, this kind of similarity can be attributed to the similar heating rates used in the literature and the present work.

3.2. Validation of the master sintering curve

From the knowledge of the activation energy of sintering as obtained above, MSC for α-Al_2O_3 has been constructed (Fig. 5). In Figure 6, the shrinkage versus isothermal hold time of ca. 6 h is shown for the samples sintered at 1200, 1350 and 1500 °C, respectively. In this plot, the abscissa represents the isothermal hold on time. From the dilatometric data of a particular run, the Θ values are calculated for the isothermal hold by Eq. (1). These values are shown on the master sintering curve as shown in Fig. 7. It can be seen that the values for all the three temperatures with different periods of time lie on the MSC, validating the concept of MSC. For clarity only a few representative data points are shown.

In addition, based on the experimental data (the density determined by the Archimedes method with different heating procedure), the relationship of ρ and Θ, shown in Fig. 8, was highly consistent with the MSC. The constructed MSC agreed

well with the densities determined by the Archimedes method under different heating history, which further verified its validity.

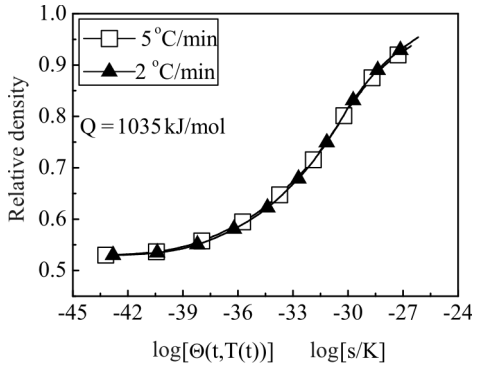

Fig. 5. MSC constructed from the sintering data shown in Fig. 2 using the activation energy of 1035 kJ/mol

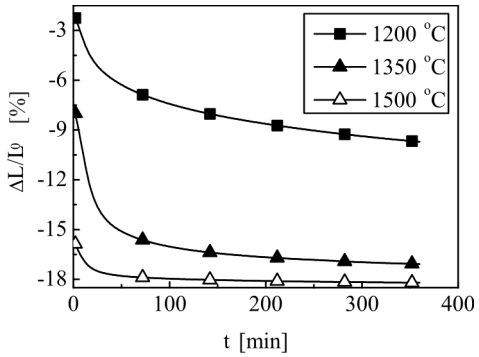

Fig. 6. The shrinkage curves for α-Al_2O_3 compacts during the isothermal heating

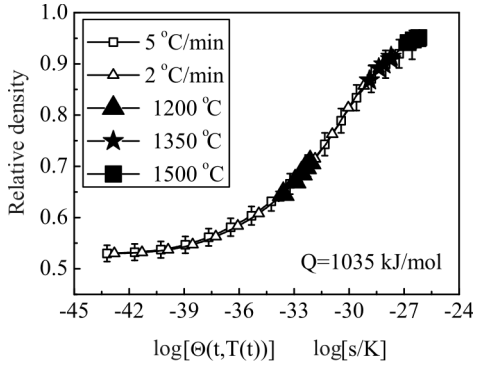

Fig. 7. Validation of MSC for α-Al_2O_3. The experimental values for three temperatures are shown (including error bars)

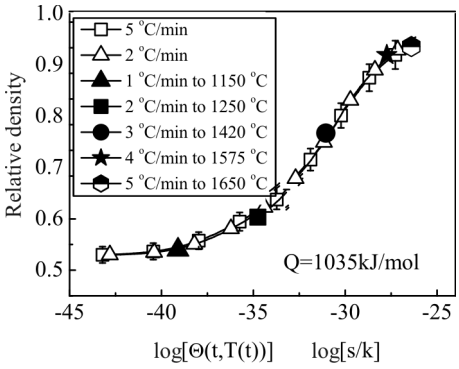

Fig. 8. Validation of MSC for α-Al_2O_3. The densities determined by the dilatometer trace are in a good agreement with the Archimedes densities (including error bars)

Thus it can be regarded that integration of the proposed sintering time –temperature profile yields a point on the MSC curve. The expected density can be obtained by finding the ordinate value at that point. On the other hand, if the final desired density is known, it is possible to find out the corresponding Θ value from the abscissa of the master sintering curve and thereafter to plan the sintering schedule [20, 21]. Thus MSC can be a characteristic measure of the sinterability of a powder compact over a wide range of densities.

4. Conclusions

Based on the constant heating rate sintering containing low heating rates only, the master sintering curve for α-Al_2O_3 has been constructed with the help of a combined-stage sintering model. A comparison between the predicted and the experimental shrinkage curves showed good consistency, thus confirming that it is possible to control shrinkage behaviour using the MSC. With one experimentally determined temperature dependent parameter Θ, the densification behaviour for α-Al_2O_3 can be described from the early to the final stages of sintering.

The concept of MSC has been used to calculate the apparent activation energy for densification during sintering for sub-micron-sized α-Al_2O_3 powders. The activation energy was determined to be 1035 kJ/mol, which is higher than the value reported by other researchers. So the evaluation of sintering activation energy based on MSC will be influenced by the heating rates.

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