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Silicon oxycarbide ceramics with reduced carbon by pyrolysis of polysiloxanes in water vapor

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Abstract

SiOC ceramics pyrolyzed from polysiloxanes are usually black because of the formation of excess carbon in the ceramic network. Here we show that the pyrolysis of polysiloxanes in water vapor significantly reduces carbon from SiOC and yields a white SiOC ceramic. Chemical analysis shows the amount of carbon in the white ceramic is only half of that in the black one pyrolyzed in argon. ^{29}Si nuclear magnetic resonance spectral (NMR) analysis indicates the reduction of the carbon-rich [SiC_4] and [SiC_2O_2] units with the enhanced formation of the oxygen-rich [SiO_4] and [$SiCO_3$] units by the water pyrolysis. Importantly, this water pyrolysis resultant carbon reduction is realized in a bulk polysiloxane, and the white SiOC ceramic is obtained in a bulk body with the retained shape of the precursor body. The water pyrolysis can be adopted as an effective mean to tailor the structure of PDCs via the simple introduction of water vapor in pyrolysis.

Keywords: White SiOC; Carbon reductions; Water; Polysiloxanes; Pyrolysis; SiOC

1. Introduction

Polymer-derived ceramics (PDCs), such as SiCN, SiBCN and SiOC, have high temperature properties and structural stabilities, promising for applications in high temperature areas.[1–3] The control of compositions and structures of PDCs is important for the development of high temperature properties and applications of PDCs.[1–3] Carbon, as the most common element in PDCs, exists both in the ceramic network as a bonding atom and in a free form as a structural unit in PDCs.[4–7] These network and free-carbon play important roles in the building of the PDC structure, and, to a certain extent, dominate the mechanical and thermal properties of PDCs. In this regard, the control of the formation and structure of carbon in PDCs is of interest on both fundamental and technical grounds. Studies indicate that the existence of free-carbon in PDCs affects the high temperature resistant and mechanical properties of PDCs.[8–12] Many studies address the reduction of free-carbon from PDCs through the designs of precursors[9,13,14] and the control of pyrolysis.[9,15]

Silicon oxycarbide (SiOC) is a typical kind of PDCs which has been widely studied in recent years because of its enhanced high temperature properties comparing to silica.[9,13,16,17] SiOC ceramics with various compositions have been produced from siloxane based sol–gel reactions and from polysiloxanes by pyrolysis.[18] Similar to other PDCs, these SiOC ceramics always contain excess amounts of carbon[16,19] because of the enrichment of carbon in the functionalities in the (poly)siloxane precursors.[18] The reduction of free-carbon from SiOC has been conducted using (poly)siloxane precursors with less-carbon or carbon-free groups (Si–CH_3, Si–H or Si–Si),[9,10,13,14,20] introducing active metal fillers or compounds (such as Ti, Al and MoSi) into polysiloxanes to react with the carbon precipitated in the precursor during pyrolysis,[21,22] and using active gases (such as ammonia) during pyrolysis of polysiloxanes or through post-annealing of SiOC ceramics.[9,15] These processes show some effects on the adjusting of the amount of carbon in SiOC, but the effect appears limited since the obtained SiOC ceramics are exclusively black.[9,18]

In this work, we report a highly efficient and simple way to reduce carbon from SiOC, that is, to pyrolyze a polysilox-

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ane in water vapor. The pyrolysis is conducted by introducing a certain amount of water during the pyrolysis of a crosslinked polysiloxane in an argon flow. In this way, we have obtained a "white" SiOC ceramic. Chemical analysis confirms the significantly reduced carbon from the water pyrolysis as comparing with that in a black SiOC pyrolyzed in argon. Apart from the suppressing of free-carbon, the water pyrolysis alters the network configuration of SiOC. ^{29}Si NMR spectral analysis indicates the reduction of the carbon-rich [SiC_4] and [$Si_2C_2O_2$] units in the water pyrolysis with the enrichment of [SiO_4] and [$SiCO_3$] units in the resultant white SiOC ceramic. Importantly, the water reduction of carbon is realized in a crosslinked bulk polysiloxane with the white SiOC ceramics achieved as a shaped bulk body with good bonding quality. The water assisted pyrolysis could become as an effective mean to reduce free-carbon in oxygen-containing PDCs with promising improved properties.

2. Experimental

The precursors for SiOC are polyhydromethylsiloxane (PHMS) ($(CH_3)_3$–[$SiHCH_3$–O–]$_m$–[$Si(CH_3)_2$–O–]$_n$–($CH_3)_3$, Kaihuasantai Co., Ltd., QuZhou, China) and tetramethyltetravinylcycletetrasiloxane (D_4Vi) ((CH_3CH=CH_2Si–O)$_4$, Zhejiang Sanmen Qianhong Co. Ltd., TaiZhou, China). Methyl-terminated polydimethylsiloxane (PDMS) ($(CH_3)_3$–[$Si(CH_3)_2$–O–]$_m$–($CH_3)_3$, Tianjin Kewei Co. Ltd., Tianjin, China) was used as an additive. PHMS and D_4Vi are crosslinkable under heating in the presence of a metal catalyst. Platinum-divinyl tetramethyldisiloxane complex, Pt[($ViMe_2Si)_2O$][$ViMe_2SiOSiMe_2$–OH], Shenzhen Anpin Silicone Materials Co. Ltd., Shenzhen, China) was used as a catalyst.

In a typical experiment, an equal amount of PHMS (6 g) and D_4Vi (6 g), 1 wt.% Pt-catalyst and 4 g PDMS were added in sequence into a flask, magnetically stirred into homogeneous. The mixture was filled in a mold (glass mold: ϕ 23 mm × 8 mm and Teflon mold: ϕ 20 mm × 10 mm), and placed into an oven at 80 °C to crosslink for 3 h. Shaped polysiloxane body was obtained after demolding. The crosslinked polysiloxane body was placed in the central position of a quartz tube located in a horizontal tube furnace. After purging the system with argon, and keeping argon flowing through the quartz tube at 150 sccm, the furnace temperature was raised at a heating rate of 15 °C/min. As the temperature increased to 500 °C, distillated water was injected into the argon flow an injection rate of 10 ml/h through a syringe driven by a pump. The corresponding concentration of water in argon is 0.12 mol.%. When the temperature increased to 1000 °C, it was kept for 1 h and cooled down at 5 °C/min. In order to know the effect of water, comparable experiments were conducted by pyrolysis of the polysiloxanes at 1000 °C in an argon flow without water using the same heating program. The pyrolysis in water was also conducted by inputting water vapor at other temperatures between 500 and 1000 °C for understanding the role of water on the reduction of carbon at different pyrolysis temperatures.

The SiOC ceramics pyrolyzed in H_2O and Ar were powdered and analyzed by ^{29}Si solid nuclear magnetic resonance spectra (^{29}Si NMR) (Infinty plus 300WB, Varian, USA). The analysis was conducted using the magic angle spinning technique (MAS) with spinning rates of 4 kHz and proton decoupling. A single pulse excitation was used with the pulse length of 4 μs and pulse delay time of 20 s. The number of accumulations is 800 and tetramethylsilane (TMS) was used as the standard for calibration. Fourier transmission infrared spectroscopy (FTIR) (Bio-Rad FTS 6000, Hercules, USA) was recorded in the region between 400 and 4000 cm^{-1} with spectral width is 2 cm^{-1} and the resolution is 0.85 cm^{-1} using powdered SiOC in KBr pellets. Microstructures were observed by scanning electronic microscopy (SEM) (Philips XL30, Eindhoven, the Netherlands). Crystal structures of SiOC ceramics were analyzed by X-ray diffractometry (Rigaku D/max 2000PC, Cu Kα, Tokyo, Japan). Densities were measured by Archimedes method using water as medium. Elemental compositions for [C] and [O] were measured using [O]/[N] analyzers (LECO TC-436, 2500 °C in helium (O/N), St. Joseph, Michigan, USA) and [C] analyzer (LECO TC-412, St. Joseph, Michigan, USA). The weight percentage for [Si] in SiOC was calculated by subtracting the contents of [C] and [O] from the unit.

3. Results and discussion

The SiOC ceramics obtained previously by pyrolysis of polysiloxanes are exclusively black, due to which, they are named as "black glass".[18] By pyrolysis of polysiloxanes in the presence of water vapor, we have obtained a "white" SiOC ceramic. Fig. 1a shows the appearance of a white SiOC ceramic obtained by pyrolysis of the polysiloxanes in argon gas mixed with water vapor. Fig. 1b shows the cross-section of a broken half of a white SiOC ceramic indicating that the white color across the whole ceramic body. When without water introduced, the pyrolysis of the polysiloxanes in argon gives a normal black SiOC, as the one shown in Fig. 1d, obtained by pyrolysis in pure argon at 1000 °C. This distant different appearance of SiOC ceramics indicates the tremendous effect of water on reducing carbon from SiOC ceramics.

The atomic bonding configuration of the white SiOC ceramic is analyzed by ^{29}Si NMR spectroscopy. The ^{29}Si NMR spectrum is shown in Fig. 2, stacked with that from the black SiOC ceramic for comparison. The black SiOC shows four chemical shift peaks at −10, −32, −72, −106 ppm with similar intensities. These peaks can be assigned to the SiC_4, SiC_2O_2, $SiCO_3$ and SiO_4 units respectively, according to the literature.[21,23] Differently, the white ceramic shows only two distinct chemical shift peaks: one at −106 ppm due to SiO_4 and another at −72 ppm due to $SiCO_3$ of different intensities with the former being almost three times stronger than the later. The chemical shift peak at −10 ppm for SiC_4 and −32 ppm for SiC_2O_2 as observed for the black SiOC are almost invisible for the white ceramic. This suggests that the water pyrolysis reduces these carbon-rich units (SiC_4 and SiC_2O_2) from the SiOC network with the enhanced formation of SiO_4 units. Therefore, the pyrolysis in water not only reduces the network carbon, but also significantly alters the atomic bonding configurations of SiOC ceramics.

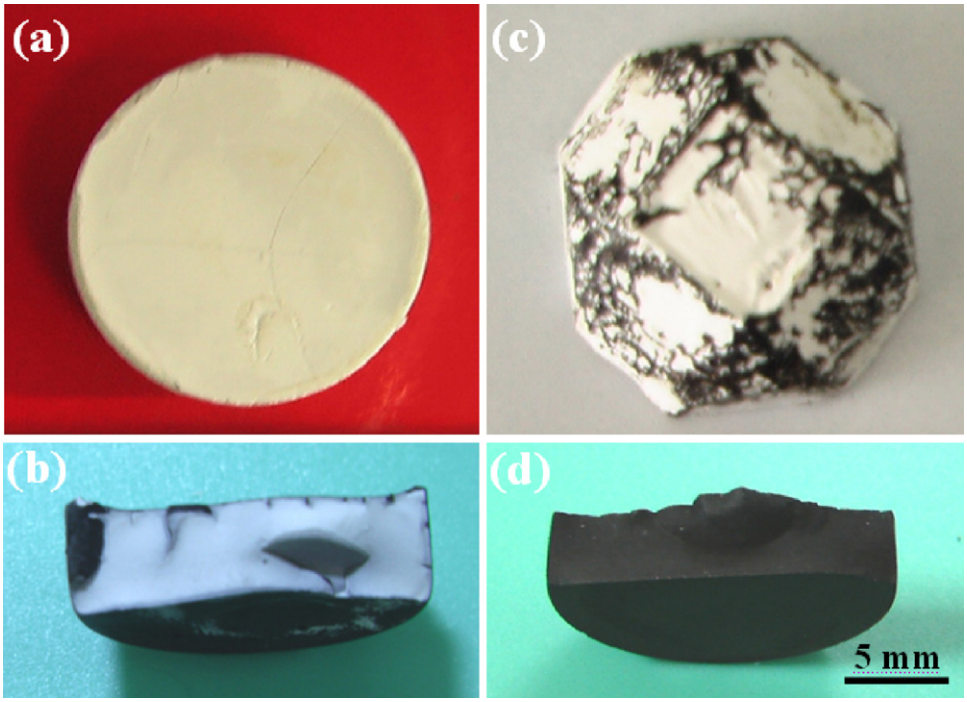

Fig. 1. Photographs of SiOC ceramics pyrolyzed from polysiloxanes in argon flow mixed with water vapor (a, b and c) and in pure argon (d). (a) A white SiOC ceramic body (dimension: ϕ18 mm × 5 mm) by pyrolysis in H_2O + Ar by inputting water at pyrolysis temperature between 700 and 1000 °C; (b) a broken piece of SiOC ceramic showing the white color across the ceramic body; (c) a SiOC ceramic body (ϕ16 mm × 8 mm) by pyrolysis in H_2O + Ar by inputting water at 1000 °C. This ceramic is black and covered with a thin layer of white phase on the surface. (d) A black SiOC ceramic by pyrolysis in pure argon at 1000 °C for comparison with (a).

X-ray diffraction analysis shows the white SiOC ceramic is amorphous (Fig. 3). There is a diffused peak around $2\theta \approx 22^\circ$ which may indicate the existence of short range ordered silica phase or small clusters. In contrast, the XRD pattern of the black SiOC does not show this diffuse peak, indicating its origination from the water pyrolysis. The detection of the short range ordered silica phase is in agreement with the NMR result showing the enrichment of SiO_4 bonding units in the white SiOC ceramic.

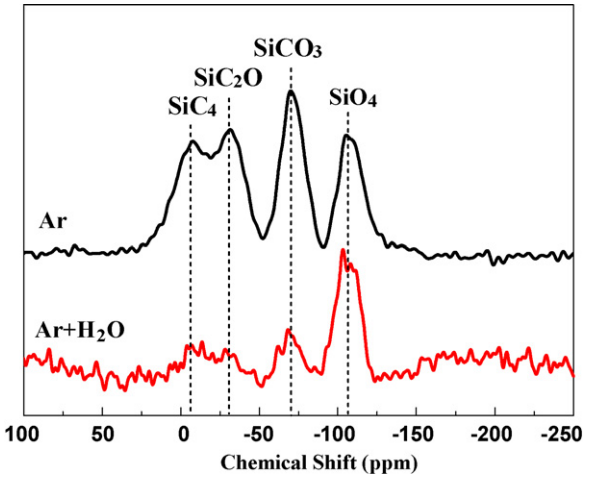

Fig. 2. ^{29}Si NMR spectra of the SiOC ceramics from polysiloxanes by pyrolysis in Ar + H_2O and in Ar.

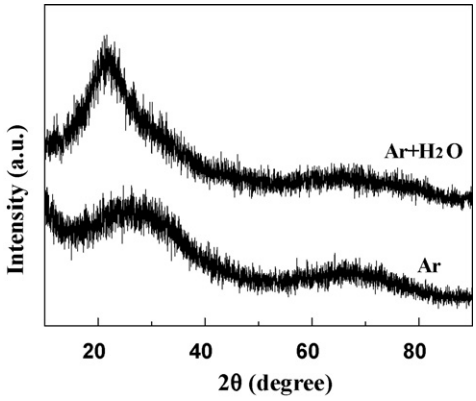

Fig. 3. X-ray diffraction patterns of SiOC pyrolyzed in Ar + H_2O and in Ar.

The compositions ([O] and [C]) of the white SiOC ceramic is analyzed by chemical analysis, as listed in Table 1, along with that of the black ceramics for comparison. The carbon content in the white ceramic is 12.12 wt.%, which is much lower than that (21.22 wt.%) in the black one. This indicates that near a half of carbon is reduced from SiOC by the water pyrolysis.

Table 1
Element analysis of SiOC ceramics formed in Ar and Ar + H_2O.

Atmosphere	C (wt%)	O (wt%)	Si (wt%)	Formula
Ar	21.22	31.32	47.46	$SiO_{1.10}C_{1.04}$
Ar + H_2O	10.12	53.37	36.51	$SiO_{2.57}C_{0.64}$

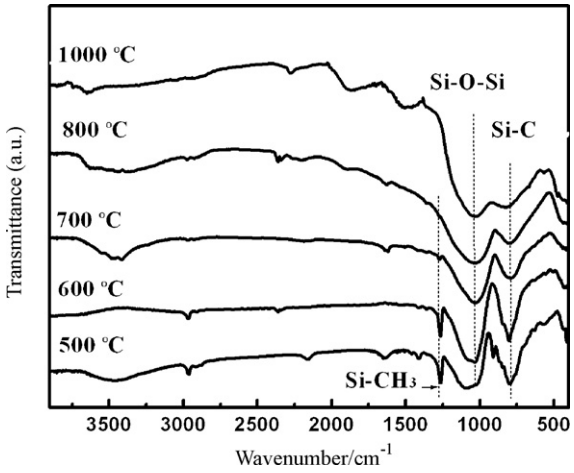

Fig. 4. FTIR spectra of SiOC from polysiloxanes by pyrolysis in Ar at different temperatures.

The oxygen content in the white ceramics is abnormally high, attaining 53.37 wt.%, as comparing to 36.51 wt.% in the black SiOC. The empirical formula for the white SiOC is calculated to be $SiO_{2.57}C_{0.64}$. The atomic ratio of [O]/[Si] (2.57) greater than that for SiO_2 is rarely observed for SiOC pyrolyzed under normal pyrolysis conditions. The large [O]/[Si] atomic ratio with respect to SiO_2 may suggests the existence of C–O bonds in the white SiOC ceramic. Silva et al. predicated the existence of a stable ternary phase of Si_2O_6C in the Si–O–C system by molecular dynamics calculations.[24] The composition of our white SiOC is equivalent to $Si_2O_{5.14}C_{1.28}$. Whether this white SiOC ceramic associates with this ternary phase has not been identified by XRD and NMR because of its quite similar structure with silica,[25] which requires further detailed structural studies.

The white SiOC ceramic can be obtained by the pyrolysis in water vapor at different temperatures between 500 and 700 °C. This temperature range corresponds to the major stage of organic-to-inorganic transformations for polysiloxanes. Fig. 4 shows Fourier transform infrared spectra of the pyrolyzed products in argon flow without water at different temperatures. The major organic groups in the pyrolyzing polysiloxane between 500 and 700 °C are Si–CH_3 (1250 cm^{-1}) and Si–CH_2–Si (1360 cm^{-1}).[26] The former (Si–CH_3) is retained from that in the precursor molecules because it resists to temperatures above 500 °C, and the latter (Si–CH_2–Si) is formed through the hydrosilylation of Si–H (in PHMS) and Si-vinyl (in D_4Vi) which proceeds below 500 °C.[16] It can be deduced that the water–carbon reduction occurs mainly through the attacking of these two groups by water molecules at the pyrolysis temperature (500–700 °C).

The possible water–carbon reduction reactions include

$$Si–CH_3 + H_2O = Si–OH + CH_4 \quad (1)$$

$$Si–CH_2–Si + H_2O = Si–OH + Si–CH_3 \quad (2)$$

because these reactions are thermodynamically favored between 500 and 700 °C.[27] The reactions between Si–CH_3/Si–CH_2–Si and H_2O produce Si–OH bonds, and the Si–OH bonds subsequently condense into Si–O–Si by dehydrogenation: Si–OH + HO–Si=Si–O–Si + H_2O. These reactions deplete Si–C bonds and form more Si–O bonds in the resultant SiOC network. The reduction of Si–C bonds from polysiloxanes suppresses the precipitation of carbon in the subsequent pyrolysis at higher temperatures.

Actually, free-carbon has started to precipitate at pyrolysis temperature below 700 °C. The water vapor has also reduced this part of carbon from the SiOC network. The reduction of free-carbon could be due to the water carbon reaction: C (s) + H_2O (g) = H_2 (g) + CO (g) which is thermodynamically favored at a higher temperature.[28]

When the water pyrolysis is conducted at a higher temperature above ~800 °C, the resultant ceramic is black in the inner body. Fig. 1c shows a SiOC ceramics obtained by the injection water at 1000 °C. A thin layer of white fluffy deposits of silica phase was formed on the ceramic surface indicating the ceramic is oxidized only at the surface layer. The ineffectiveness of water–carbon reduction at the higher pyrolysis temperature is probably due to the elimination of most organic groups above 800 °C, as seen from the FTIR spectra (Fig. 4).

It is valuable that the water carbon reduction is achieved in a bulk polysiloxane. This is different from the previous pyrolysis work involving other active gases that is mostly conducted in powdered materials.[9,15] The enabling reduction of carbon in the bulk material indicates that water vapor could penetrate into the polysiloxane body. The path for the water penetration should be the pores that were generated at the intermediate stage of pyrolysis due to the decomposition of volatile polysiloxane components in the precursors. At higher temperatures, say above 800 °C, water is difficult to penetrate inside the ceramic as a result of the enclosing of pores. The formation of micro-pores between 500 and 700 °C and their enclosing at higher temperatures above 900 °C was observed in SiOC ceramics during pyrolysis of polymethylsilsequioxane.[29]

The water pyrolysis does not impair the bonding quality of the SiOC ceramics. The pyrolyzed ceramic retains the shape of the precursor body without cracks. The linear shrinkage of the white ceramic is ~22%, slightly smaller than that (~26%) of the black SiOC ceramic. The ceramic yield is 71 wt.% by weighting the sample before and after water pyrolysis which is higher than that of 61 wt.% for the pyrolysis in argon as a result of the incorporation of oxygen. The decrease of shrinkage in the water pyrolysis was compensated by the weight increase. As a result, the final ceramics have a density (1.78 g/cm^3) similar to that (1.80 g/cm^3) from the argon pyrolysis. Scanning electronic microscopy observation shows the as-pyrolyzed white SiOC ceramics are dense on surfaces and fractural surfaces free micro-size pores and cracks (Fig. 5). Through this bulk water–carbon reduction process, we have achieved bulk SiOC ceramics with fairly macroscopic sizes, as the one shown in Fig. 1a, which has the dimension of ϕ 35 mm × 6 mm. This demonstrates that this water-pyrolysis strategy can be applied for the direct fabrication of shaped bulk SiOC ceramics without free-carbon. Moreover, this process could be generalized for the fabrication of oxygen-containing PDCs for the development of novel PDC structures, properties and applications.

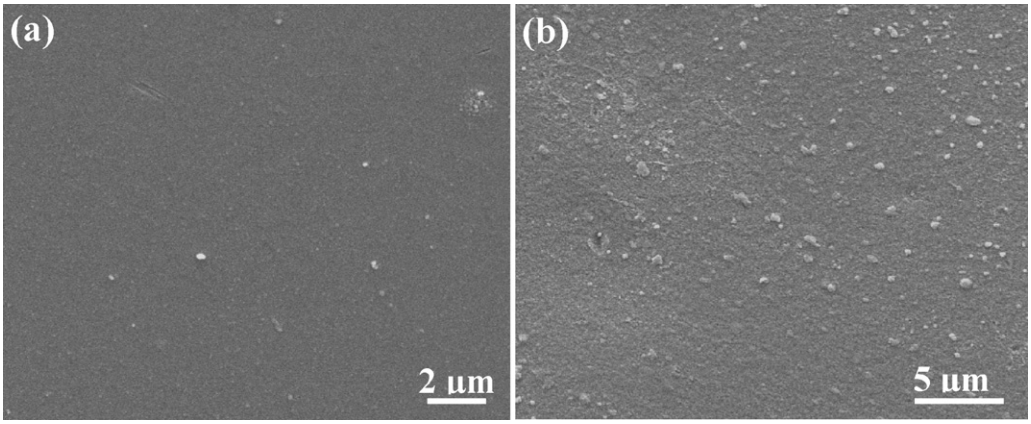

Fig. 5. Scanning electronic microscopy images of the surfaces (a) and fractural surface (b) of the white SiOC ceramics pyrolyze in $Ar + H_2O$.

4. Conclusions

The pyrolysis of a polysiloxane in water vapor can yield a white color SiOC ceramics in a certain range of pyrolysis temperature (500–700 °C). The water pyrolysis remarkably reduces the network carbon, changes the atomic bonding configurations, and suppresses the precipitation of free-carbon in the final ceramics, as analyzed by NMR spectroscopy. It appears that the water–carbon reduction proceeds through the attacking of the carbon containing organic groups, such as $Si–CH_3$/$Si–CH_2–Si$ $Si–CH_3$ by water to form more Si–O bonds in the SiOC ceramic. The water pyrolysis can be realized in bulk polysiloxane body through the penetration of water vapor into the polymeric network. This provides white SiOC ceramics that retain the shape and bonding quality of the precursor body without cracks. This water–carbon reduction strategy can be applied to tailor the structure of oxygen-containing PDCs for the improvement of materials properties or the development of new PDC materials.

Acknowledgments

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