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Synthesis of ceramic oxide powders by microwave plasma pyrolysis

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Ceramic powders prepared pyrolytically exhibit homogeneity and, in most cases, small grain sizes. The energy efficiency of electrically heated systems performing the pyrolysis in a stream of carrier gas is poor. Similar considerations concerning energy demand are valid for spray drying of suspensions. This situation can be improved using a microwave plasma as a source for thermal energy. The process described in this paper works with any aqueous solution of salts used as starting material in ceramics. The process was demonstrated by the synthesis of alumina, zirconia, and zirconia-based ceramic powders; where an energy efficiency of more than 80% was found. For the powder synthesis, aqueous solutions of the nitrates were used as starting materials. Through proper selection of conditions for synthesis, it is possible to obtain nanocrystalline powders, as demonstrated by electron microscopy. Because of the extreme conditions associated with plasma during synthesis, it is possible to prepare non-equilibrium structures and solid solutions in systems in which nearly no equilibrium solubility exists.

1. Introduction

In the synthesis of ceramic powders, two major issues are involved. In synthesizing ceramic powders it is difficult to obtain homogeneous material, especially in the case of complex compositions. It is nearly impossible to achieve this goal by mechanical blending and grinding processes. In the case of chemical precipitation processes it is very difficult to obtain homogeneous powders because often the various constituents precipitate at different pH values. This problem can be overcome by using pyrolytic processes [1–4]. Even when pyrolytic methods are best suited for the synthesis of complex ceramic powders, the demand on energy for those methods is a major concern. The same problems concerning energy demand are valid in the case of spray drying of suspensions. This problem is most important in electrically heated systems. The use of a flame as a source of thermal energy improves the situation significantly [1, 2, 4].

Using a microwave plasma as a source of thermal energy, it is possible to minimize drawbacks for pyrolytic synthesis of ceramic powders. The energy efficiency of flame processes cannot be reached, because flame processes are not impaired by the second law of thermodynamics, as is the case with all processes using electrical energy. In contrast to flame processes, the application of a plasma has the advantage that it is not necessary to account for the chemistry and the safety of a flame. Direct coupling of microwaves to a mist of a salt solution does not lead to the intended product, because the coupling of microwaves with frequencies up to 2.45 GHz to the small droplets is not strong enough [5, 6].

Plasma processes for pyrolytic synthesis of ceramic powders are described frequently. These processes are usually either working with a d.c. or an r.f. plasma, with temperatures between 5000 and 15 000 °C. In other cases, r.f. plasma methods employ gas-phase reactions in glow discharges and at low pressures. The production rate is limited significantly at low pressures (e.g. < 1 mbar). In addition, this kind of process does not lead to completely reacted products [7].

2. Experimental procedure

A microwave plasma is heated by transfer of energy to a charged particle in an oscillating electric field. This energy transfer is inversely proportional to the mass of the charged particle and inversely proportional to the square of the frequency. With microwaves, the frequency is high, so the amount of energy transferred to the ions is small. A substantially higher amount of energy is transferred to the electrons and thus to the ions, because their mass is diminishingly small. So energy transfer to the ions is primarily caused by elastic and inelastic collisions with the electrons. The "temperature" of the free electrons is much higher than the "temperature" of the ions. As the energy of the electrons can be controlled by the strength of the electric field and the collision frequency, the temperature of a gas passing a microwave plasma can be adjusted by properly selecting field strength, gas pressure and gas species. Usually a stable microwave plasma can be obtained in a temperature range between 400 and 900 °C. Temperatures given in this paper are the temperature of the plasma gas after passing the plasma zone. Gas pressure and temperature needed for the synthesis of significant amounts of ceramic powders can be varied in a range optimal for chemistry and production rate. For the synthesis of oxide ceramic powders, air, argon, helium, or mixtures of those noble gases with oxygen can be used as plasma gas. Additions of oxygen increase the temperature of a noble gas plasma; air leads to the highest plasma temperatures.

The plasma was created in a reaction vessel made of quartz glass, placed in a resonance cavity connected to a microwave generator. The cavity was part of a WR 975 waveguide system using the TE_{10} mode. A standing wave was adjusted using a sliding short circuit. A microwave generator with a frequency of 0.915 GHz was used.

The solutions were sprayed into the plasma zone using a two-phase nozzle. The nozzle applied delivers a mist of droplets with a mean diameter of about 7 μm [8]. The temperature of the gas was monitored after passing the reaction (plasma) zone. The powder synthesized was collected after measuring the temperature.

3. Results

3.1. Morphology of the powder

The ability of a microwave plasma to act as a source of heat for powder synthesis was demonstrated by the production of ceramic powders based on zirconia and alumina. Aqueous solutions of nitrates were used for those experiments. Typically, a gas volume of about 5–10 m^3h^{-1} passed the plasma zone carrying a mist of the aqueous solution of the reactants equivalent to a volume between 0.5 and 1.0 lh^{-1}. A broad range of experimental conditions was explored to study the influence of the synthesis parameters on the powder morphology. The results of five typical runs are described below (Examples 1–5) showing the variability of the powder structure achieved. The experimental details from each run are collected in Table I.

3.1.1. Example 1

In this experiment, pure zirconia was prepared. Electron microscopy revealed particle sizes in the range of about 100 to about 500 nm. The particles are spherical; large particles are broken into pieces. Crystallite sizes are less than 50 nm, but most particles exhibit crystallite sizes of less than 10 nm. Fig. 1 exhibits some typical spherical particles with crystallite sizes less than 10 nm. The majority of the particles are crystallized in the cubic fluoride structure and are not transformed to the equilibrium modification. Nevertheless, a few particles exhibiting tetragonal or monoclinic structure were also found. Amorphous particles were not found.

3.1.2. Example 2

The synthesis of ZrO_2–Y_2O_3–Al_2O_3 ceramic powder resulted in single-phased, cubic zirconia. Segregation

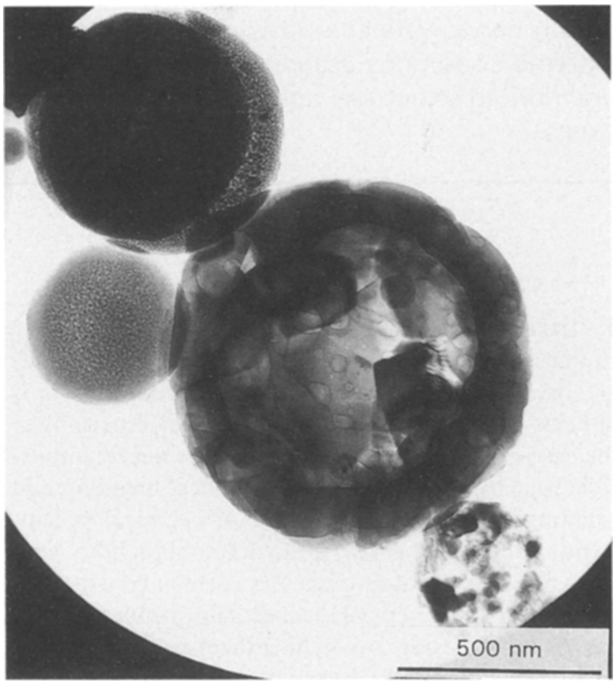

Figure 1 ZrO_2 powder particles synthesized in an argon microwave plasma from the nitrate. Except for one hollow particle, all the particles exhibit grain sizes below 10 nm.

TABLE I Experimental conditions for powder synthesis. Frequency 915 MHz

	Example				
	1	2	3	4	5
Composition of the product (mol %)	ZrO_2	77 ZrO_2 3 Y_2O_3 20 Al_2O_3	77 ZrO_2 3 Y_2O_3 20 Al_2O_3	77 ZrO_2 3 Y_2O_3 20 Al_2O_3	Al_2O_3
Concentration of nitrates in water (mol^{-1})	0.5	0.1	0.1	0.1	1.0
Plasma gas	Ar	Ar 20 vol% O_2	He	Air	Air
Pressure mbar	133	133	156	94	96
Flow rate STP (m^3h^{-1})	9	9	12	6.5	6.5
Temperature (° C)	450	550	650	750	750

of zirconia and alumina was not observed. Similar to the case of pyrolysis in a hydrogen flame, alumina is in a non-equilibrium solid solution in zirconia [1, 2]. Particle sizes are found to be in the range 100–1000 nm. As shown in Fig. 2, most of the particles exhibit crystallite sizes of less than 10 nm, in this case crystallite sizes up to 50 nm were found. The majority of the particles were observed to be solid; a few were hollow.

3.1.3. *Example 3*

This synthesis of ZrO_2–Y_2O_3–Al_2O_3 ceramic powder in helium carrier gas produced single-phase cubic zirconia. A small fraction of amorphous particles was observed. Particle sizes were in the range 100–1000 nm. Crystallite sizes were less than 10 nm. In this case, only a few particles were hollow. Segregation of zirconia and alumina was, as in Example 2, not observed. Fig. 3 shows some powder particles with crystallite sizes less than 10 nm. One of the particles is amorphous, characterized by the absence of any structure in the micrograph.

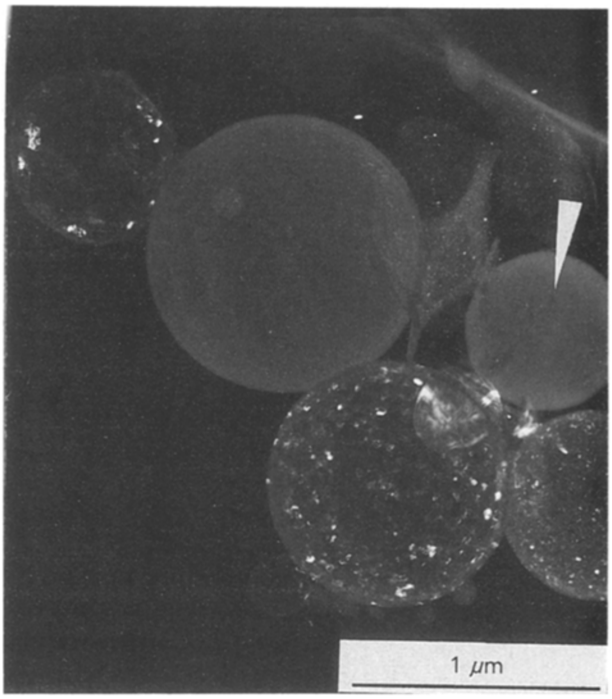

Figure 3 ZrO_2–Y_2O_3–Al_2O_3 powder synthesized in a helium microwave plasma. Crystallite sizes are less than 10 nm. The particle indicated by an arrow is amorphous.

3.1.4. *Example 4*

This experiment to obtain ZrO_2–Y_2O_3–Al_2O_3 ceramic powder was performed in air as plasma gas. The powder delivered was again single-phase cubic zirconia. The start of segregation of the various constituents was observed. Some of the alumina remained in a non-equilibrium solid solution in zirconia. Amorphous particles were not observed. Particle sizes were in the range 100–1000 nm. Crystallite sizes were less than 40 nm. The majority of the particles were found to be solid; a few were hollow. A typical example of an initial phase separation of zirconia and alumina is shown in Fig. 4, which indicates an increase of the concentration of a lighter (brighter phase in this bright-field image) phase in the centre and on the surface of the particle. This seems to be the typical pattern of initiation of segregation. The most important outcome of this example is the fact that it is not necessary to use any noble gas for generation of a stable plasma.

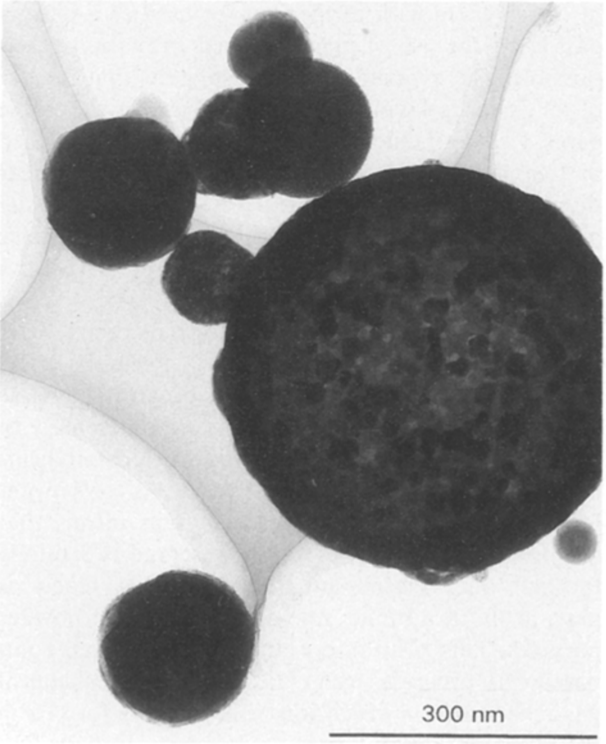

Figure 2 ZrO_2–Y_2O_3–Al_2O_3 powder synthesized in an argon–oxygen microwave plasma. Crystallite sizes are less than 10 nm.

3.1.5. *Example 5*

This synthesis of Al_2O_3 ceramic powder delivered single-phase cubic product in the gamma phase (spinel structure). Amorphous particles were not observed. Particle sizes were in the range 100–2000 nm. Crystallite sizes were about 40 nm. The majority of the particles were found to be solid; however, more hollow particles were found than in the previous examples. Fig. 5 gives typical examples for the product obtained.

3.2. Energy balance

A determination of the energy balance in a microwave plasma system was performed to check the energy efficiency. Experimental conditions were not selected

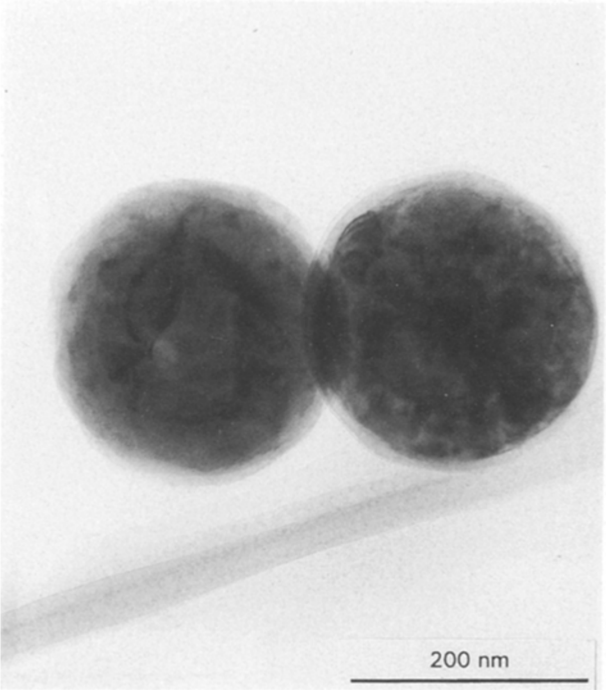

Figure 4 Two particles of a ZrO_2–Y_2O_3–Al_2O_3 powder synthesized in an air microwave plasma. The less dense layer around the spheres consists of Al_2O_3. This indicates the beginning of the segregation between ZrO_2 and Al_2O_3.

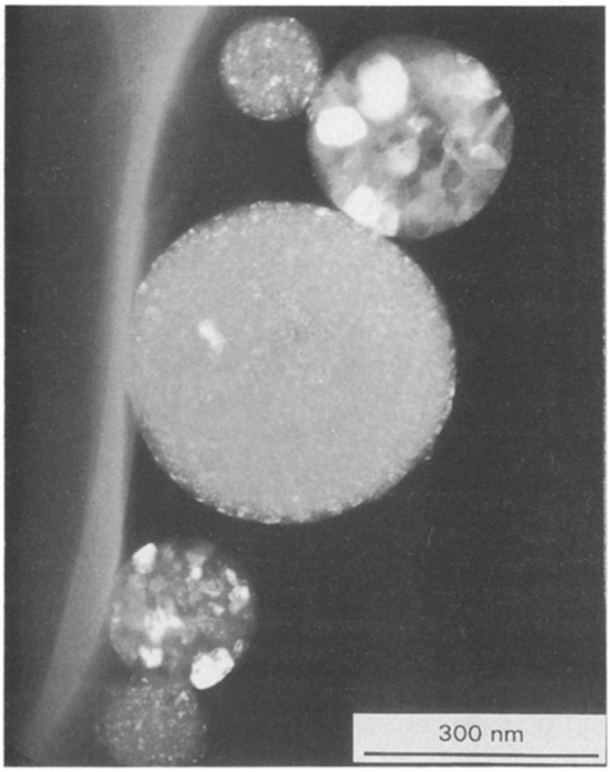

Figure 5 Particles of an Al_2O_3 powder synthesized in a microwave plasma from a nitrate solution. Crystallite sizes are about 40 nm.

on optimal points of operation; rather, very stable conditions were selected, allowing a broader range of gas flow and injection of water. The following data were obtained [9]:

Energy requirements:

Energy to heat the carrier gas up to 750 °C

$1.2\ \mathrm{l\,s^{-1}}$ Ar	805 J
$0.3\ \mathrm{l\,s^{-1}}\ O_2$	314 J

Evaporation of the water and heating up to 750 °C

$0.22\ \mathrm{g\,s^{-1}}\ H_2O$ 805 J

Total energy requirement:	$2034\ \mathrm{J\,s^{-1}}$
Total energy input:	$2440\ \mathrm{J\,s^{-1}}$
Reflected energy:	$220\ \mathrm{J\,s^{-1}}$
Energy losses in the cavity:	$186\ \mathrm{J\,s^{-1}}$

In the experiment described, 83% of the microwave energy input was used for the process. The energy losses in the cavity are attributable to ohmic losses in the cavity and, to a minor extent, to radiation of the plasma. The overall efficiency could be increased by using a cavity made of copper instead of stainless steel. Of the energy, 9% was reflected in the case discussed. It is possible to reduce the amount of reflected energy to less than 1.5% using a tristub tuner. Under these conditions, a motor-driven readjustment of the tuner according to changes in the process is required during operation. For a final judgement the efficiency of the conversion of electrical energy to microwave energy of about 90% (assuming a 60 kW, 0.915 GHz generator [10]) has to be taken into account.

4. Discussion

It has been proven that it is possible to use a microwave plasma as a source of thermal energy for a pyrolysis reaction to synthesize ceramic powders with high-energy efficiency. Pure noble gases or a mixture of one of them with oxygen can be used as a plasma gas. Even the use of plain air used as plasma gas is possible. The experimental data suggests that the use of air is more favourable than the use of the noble gases. Using air, additional nitric oxides are produced in the plasma. However, in the special case under discussion, in which nitrates were used as starting materials, this cannot be considered as a disadvantage, as the process of pyrolysis of nitrates itself produces a significant amount of nitric oxides.

A comparison of the morphology of the powder particles obtained by plasma pyrolysis with the morphology of powder particles obtained by flame pyrolysis [1, 2], indicates virtually no differences. In this respect, the two processes are equivalent, indicating that the mechanisms of the reactions for powder formation are essentially identical. This means that the process of plasma pyrolysis observed is a purely thermal one. Plasma-enhanced chemical reactions play, at most, a minor role at the surface of powder particles. This is an important difference when compared with processes using plasma-enhanced chemical gas reactions, for which ions and radicals formed in the plasma are essential.

The structure of the powders obtained by plasma pyrolysis are, in all cases, not in thermodynamic equilibrium. Zirconia-based material was found to be cubic, which is the high-temperature structure of zirconia. This might have been expected, as, according to Ostwald's rule, crystallization always starts with the phase stable at the highest temperature. The transformation to the phases stable at lower temperatures is thwarted by the small size of the crystallites, which is usually less than 10 nm. The small crystallite size stabilizes the denser high-temperature structure through compressive stresses induced by surface tension at room temperature. The phase diagrams give no indication of a stabilization of the cubic fluorite structure by alumina [11]. A transformation at the high temperature in the plasma is certainly impossible, as the residence time in the plasma is estimated to be between 2 and 6 ms. Similar observations were made by Hahn *et al.* [12] on yttria with crystallite sizes about 7 nm, which was found to have the high-temperature phase stabilized at room temperature.

In the case of alumina, explanation of the structures observed is not as easy. Alumina was found to be in the cubic phase (spinel structure). This cubic phase usually transforms at temperatures between 800 and 1200 °C into the rhombohedral (sometimes called "hexagonal") phase [13]. This rhombohedral phase is stable up to the melting point. This finding seems to be in contradiction with Ostwald's rule. Similar to all other cases, where this rule was found to be valid, the cubic phase of alumina is the phase with the highest symmetry. In addition, it must be taken into account that gamma alumina might be an oxygen-deficient phase stabilized by hydrogen [13, 14].

Compared to zirconia, the alumina powder exhibits relatively large crystallites: about 40 nm. These large crystallites are not stable. Possibly they contain a large amount of lattice imperfection. This leads to spontaneous recrystallization when heated in the beam of the electron microscope. Figs 6 and 7 show an example of a spherical, single-crystal alumina particle with a diameter of about 50 nm. Heating in the electron microscope provoked recrystallization, leading to a polycrystal with crystallite sizes about 5 nm. Similar phenomena were not observed with the zirconia-based powder. In this case, it was impossible to obtain spontaneous crystallization of the amorphous particles during heating with the electron beam.

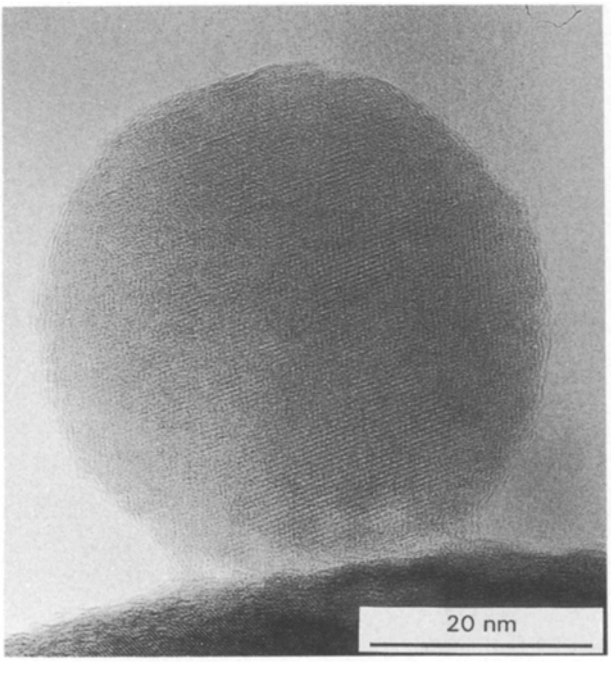

Figure 6 Small Al_2O_3 particle. From the lattice fringes one realizes that this particle is monocrystalline.

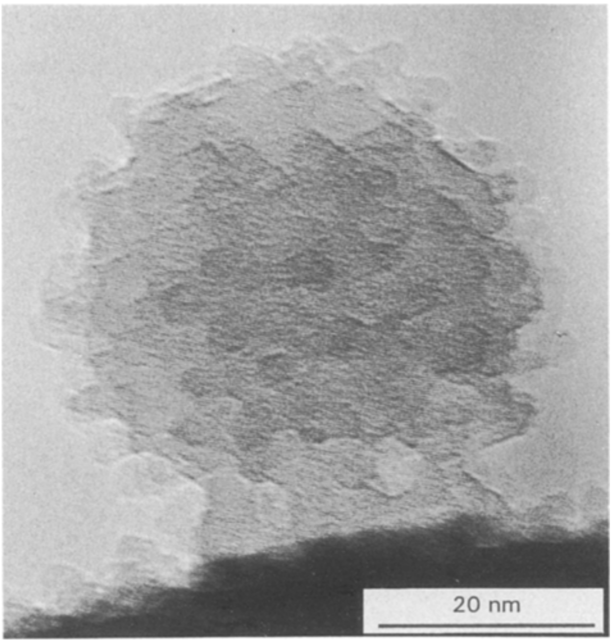

Figure 7 Al_2O_3 particle from Fig. 6. The particle recrystallized during observation in the electron microscope.

5. Conclusions

Pyrolysis of aqueous solutions to obtain nanocrystalline ceramic powders is energetically a highly efficient process. In the experiments, performed in a TE_{10} single-mode cavity, an overall efficiency of more than 80% was determined. Electric field strength, gas, and gas pressure are variables that can be used to influence the properties of the product. Air, a noble gas, or a mixture of a noble gas with oxygen can be used as plasma gas. The powder obtained was, in the case of zirconia, crystallized in the cubic fluorite structure, independent of additions of yttria or alumina. It is assumed that this structure is stabilized by the small crystallite size of less than 10 nm. In the case of alumina, the crystallite size was about 40 nm. Crystallization was in the cubic structure.

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