

Tc Carbide and New Orthorhombic Tc Metal Phase

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Tc metal and metal-like carbide phases are revisited with special attention given to Tc-rich phases in the view of prospective nuclear fuel utilization and alternative transmutation targets fabrication. A new Tc-metal phase has been found and new softer conditions for the Tc carbide formation were observed. The unit cell parameters of a new orthorhombic Tc metal were $a = 2.805(4)$, $b = 4.958(8)$, $c = 4.474(5)$ Å ($V/Z = 15.55$ Å³) for Tc-C with 1.38 wt.% C and $a = 2.815(4)$, $b = 4.963(8)$, $c = 4.482(5)$ Å ($V/Z = 15.65$ Å³) for Tc-C with 1.96 wt.% C.

1. Introduction

Tc metal-like carbide phases and mixed Tc-Ac-C and (Tc/Mo)-Ac-C carbide have got new sound in the view of prospective nuclear fuel utilization. The published data on the preparation and properties of technetium carbide are not enough sufficient for the prediction of technetium behavior in the uranium carbide nuclear fuel during and after the irradiation in nuclear reactors as well as for the consideration of the alternative to pure metal targets for technetium transmutation.¹⁻⁵ We revisited these studies with special attention given to Tc-rich phase diagram triangle. Here we report on the new Tc-metal phase found and new softer conditions of Tc carbide formation.

2. Experimental

The initial metal technetium was prepared by reduction of synthetic $(\text{CH}_3)_4\text{NTcO}_4$ in Ar-6% H₂ gas in a gas-flow tubular furnace at 500 °C followed with annealing just only at 800 °C to avoid microparticle adhesion. As the metal samples were X-ray amorphous, the ESCA spectra were applied to support the formation of Tc-metal phase (Figure 1) with reference to.⁸

The resulting Tc metal was finely grinded and the fine fraction from 20 to 50 micrometer in diameter was sieved for the experiment.

The samples of 500 mg of Tc metal were vigorously grounded together with the desired quantity of ultra-pure carbon and pressed at $p = 1$ ton/cm² giving the resulting 5 mm-thick pellets that were annealed in high temperature vacuum furnace at the temperatures 800 °C, 1000 °C and 1200 °C. The annealing temperature was achieved in 1.5 hours. Annealing time was two hours (in some cases also 8 hours) for each chosen temperature. After annealing accomplishing the samples were cooled to room temperature in vacuum during 6–8 hours. X-ray powder diffraction patterns were recorded directly from the pellet surfaces both before and after polishing.

3. Results and Discussion

The pellets with variable Tc:C atomic ratio (see Table 1) were prepared. The experiments were carried out aiming to study the interaction of Tc metal with graphite at different Tc/C atomic ratios as a function of annealing temperature.

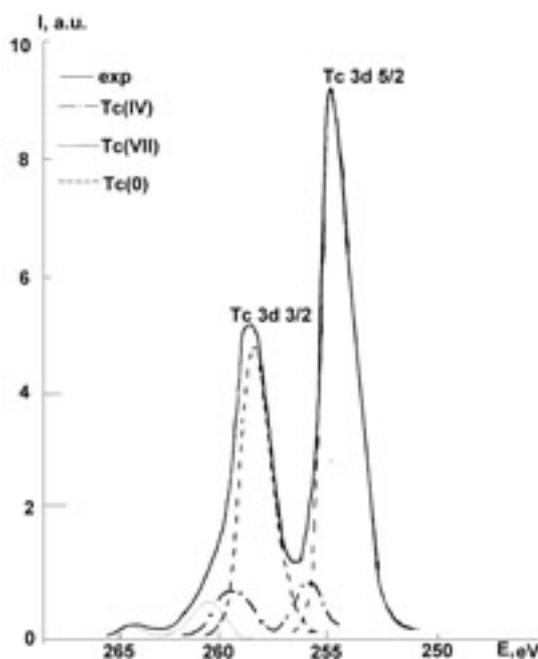


Figure 1. ESCA spectrum of the Tc_{met} prepared by reduction of $(\text{CH}_3)_4\text{NTcO}_4$ in Ar-6% H₂ gas.

TABLE 1: Experimental Set for Tc -C Pellet Preparation

Sample No	Tc, mg	C, mg	Tc, wt.%	C, wt.%
3	500	7	98.6	1.4
2	500	10	98.0	2.0
4	500	16	96.8	3.2
5	500	21	95.9	4.1
1	500	60	89.2	10.8

⁹⁹Tc NMR (Bruker MSL-300, magnetic field 7.04 T, SF = 67.55 MHz) and ESCA (HP 5950A) spectroscopy were used for the analyses of Tc speciation. ¹³C NMR (also at Bruker MSL-300) was used for the speciation of carbon (see Figure 2) inside the pellets. Microhardness measurements have been carried out with a diamond head test instrumentation and an optical microscope. The obtained results led to the conclusion on the formation of the biphasic composition that includes the technetium carbide Tc_xC where ($x > 1$, in most cases $2 < x < 6$) and the excess carbon starting from 17 at.%.

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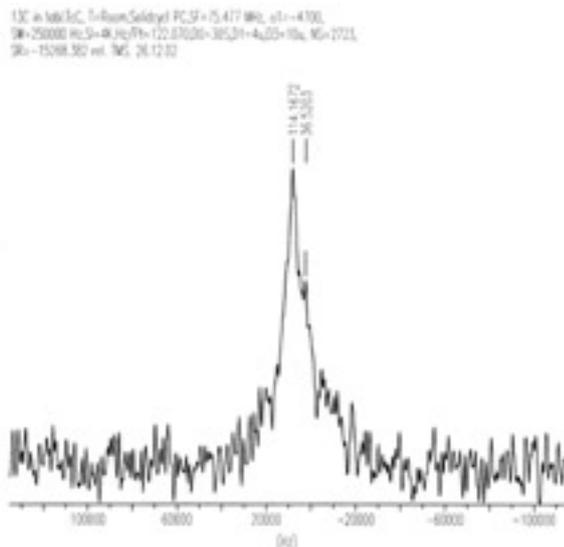


Figure 2. ^{13}C -NMR spectrum of the non-destructed pellet (sample 1, Tc:C = 1:1) of technetium carbide with graphite.

In the range of low carbon concentrations (Tc-C mixtures of 1–2 wt.% C, 10 to 15 at.% C) at 800 °C the formation of newly found intermediate orthorhombic Tc metal was proved by X-ray powder diffraction analyses (see Figure 3). The unit cell parameters were $a = 2.805(4)$, $b = 4.958(8)$, $c = 4.474(5)$ Å ($V/z = 15.55$ Å³) for Tc-C with 1.38 wt.% C and $a = 2.815(4)$, $b = 4.963(8)$, $c = 4.482(5)$ Å ($V/z = 15.65$ Å³) for Tc-C with 1.96 wt.% C. The parameters of Tc could be explained by orthorhombic distortion of the well known *hcp* Tc metal structure $a_1 = a$, $b = a_2\sqrt{3}$, $c = c$ as shown at Figure 4.

The formation of similar phases most probably has taken place under conditions used in references,^{2,4} but the distortion of the lattice parameters determined in these references for the Tc-rich phases were very much different one from another and in fact erroneous, although the parameters reported in the same references for the cubic technetium carbide and for Tc-U-C carbide phases were correct (see also the discussion in).⁹

This research shows that technetium carbide is being formed somewhat easier if compared to previously known data,^{2,4} indicating that its formation in the spent uranium carbide nuclear fuel is quite possible.

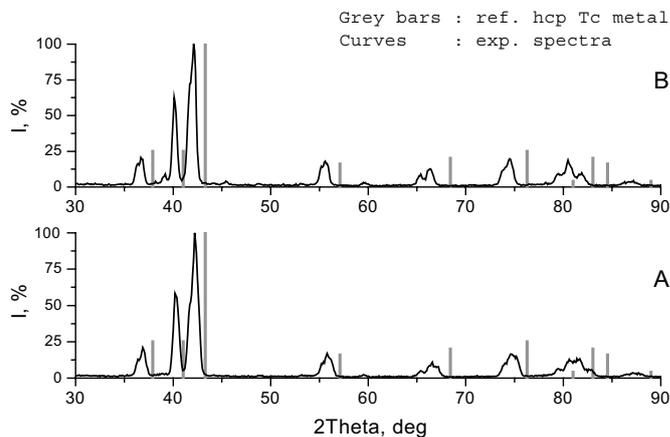


Figure 3. X-ray Diffraction spectra of pellets Tc-C annealed for 8 hours at 800 °C: **A** – 1.38 wt.% C; **B** – 1.96 wt.% C.

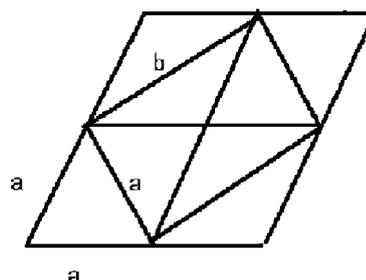


Figure 4. Transformation of the initial *hcp* Tc metal cell to the new orthorhombic cell : $a_1 = a$, $b = a_2\sqrt{3}$, $c = c$.

The *fcc* Tc carbide phase is defective in carbon. Some estimates of the boundary frames of Tc carbide composition were obtained indicating the upper limiting ratio of about Tc: C = (5 ± 0.5): 1 although the exact composition of Tc carbide could be further précised.

The X ray diffraction study proved the formation of cubic phase with $a = 3.98$ Å (Fm3m) in the interval of Tc: C ratios from 1: 1 to 5: 1. The cubic Tc carbide phase was observed already at $T = 800$ °C indicating that the conditions for its preparation could be much softer compared to that reported in.^{2,4}

Micro-hardness of Tc carbide depends on the C content and the temperature of preparation, and it is by the factor of 2–2.5

TABLE 2: Micro-hardness Measurements and X-ray Diffraction Tests for the Second Experimental Set for Tc -C Pellet Preparation (Tc mass was 500 mg in each pellet)

Samp. No	C, mg	C, wt.%	Results of physical tests (X-ray powder diffraction, cell determination, microhardness measurements) made after annealing at		
			800 °C	1000 °C	1200 °C
3	7	1.4	Tc _{met} , ortho, ↑V, H = 278 kg/mm ²	Tc _{met} , hexag., ↑V, H = 255 kg/mm ²	Tc _{met} , hexag., ↑V, H = 476 kg/mm ²
2	10	2.0	Tc _{met} , ortho, ↑V, H = 304 kg/mm ²	Tc _{met} , hexag., ↑V, H = 284 kg/mm ²	Tc _{met} , hexag., ↑V, H = 529 kg/mm ²
4	16	3.2	Tc _{met} , orto, ↑V, H = 324 kg/mm ²	Tc _{met} , hexag., ↑V, H = 281 kg/mm ²	Tc _{met} , hexag., ↑V, H = 304 kg/mm ²
5	21	4.1	Tc _x C + C, ~V, Zone 1 : H = 327 kg/mm ² Zone 2 : H = 227 kg/mm ²	Tc _x C + C, ~V, Zone 1 : H = 304 kg/mm ² Zone 2 : H = 227 kg/mm ²	Tc _x C + C, ~V, Zone 1 : H = 461 kg/mm ² Zone 2 : H = 228 kg/mm ²
1	60	10.8	Tc _x C + C, ~V, Zone 1 : H = 320 kg/mm ² Zone 2 : H = 228 kg/mm ²	Tc _x C + C, ~V, Zone 1 : H = 320 kg/mm ² Zone 2 : H = 228 kg/mm ²	Tc _x C + C, ~V, Zone 1 : H = 470 kg/mm ² Zone 2 : H = 227 kg/mm ²

- V = Unit cell volume/Z; ↑V : specific unit cell volume per atom increases, ~V : specific unit cell volume is steady
- H = microHardness.
- Tc_{met} : metal Tc is formed, ortho : orthorhombic Tc metal phase, hexag.: *hcp* Tc metal
- Tc_xC + C : a mixture of Tc carbide and graphite is present

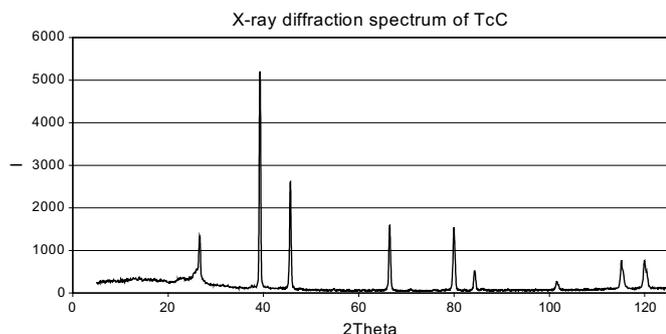


Figure 5. Experimental X-ray diffraction pattern of Tc metal annealed with 50 at.% C at 1150 °C for 8 hours (fcc TcC_{1-x} produced + $C_{x\text{rest}}$).

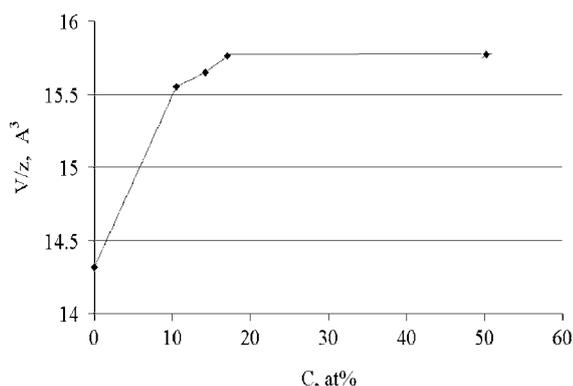


Figure 6. Tc metal/Tc carbide specific cell volume (V/z , per 1 Tc atom) as a function of C content.

higher compared to the micro-hardness of pure technetium metal and of newly found orthorhombic Tc metal phase (see Table 2).

Microanalyses of the polished section indicate the presence of two phases: 1) the white phase presents a carbon-defective technetium carbide Tc_xC where ($x > 1$, presumably ($2 < x < 6$)) while the black phase is non-reacted carbon. The X-ray pattern supported the presence of these two phases (Figure 5).

The microhardness measurements at the white parts of the pellet the 17–22% increase in comparison with *hcp*-technetium metal foil, while the microhardness measurements at black sites were characteristic of pure carbon.

Tc metal specific cell volume (per 1 Tc atom) increases by ~10% with the increase in C content from 1 to 20% and then presents a steady value (Figure 6). This is an important input data for the design of the more stable phases for the further researches.

Analogous tests were carried out with Re metal. No changes were observed in the structure of hexagonal Re-pattern, in good agreement with⁷ and the higher melting temperature of Re-metal (~3180.0 °C ~ 3453.15 °K) compared to Tc melting temperature (2157 °C, modern values for the melting points are used, the corrected melting point for technetium becomes 2430 °K. The peak of non-reacted graphite was also present in the X-ray pattern of Re-C mixture.

The attempts were undertaken to characterize the samples of technetium carbide with ⁹⁹Tc-NMR and ¹³C-NMR methods, the spectra were recorded at the non-destructed pellets. The ⁹⁹Tc – NMR spectrum of the Tc:C = 1:1 sample was of medium quality and was roughly characterized with Knight shift of 1570 ppm (with reference to 0.1 M K_2TcO_4 solution). This Knight shift is quite different from the one observed in pure Tc metal.¹⁰

The ¹³C-NMR spectrum of non-destructed pellet No 1 (with the ratio Tc:C = 1:1) (see Figure 2) gave evidence for the presence of intensive peak of non-reacted graphite at 114.16 ppm and a shoulder at 36.52 ppm that is attributed to the carbon present in the technetium carbide matrix.

Our findings are in good agreement with the predicted phase Tc-C diagram in,¹ that was based on the experimental results from²⁻⁵ and taking into account the results of calculating the

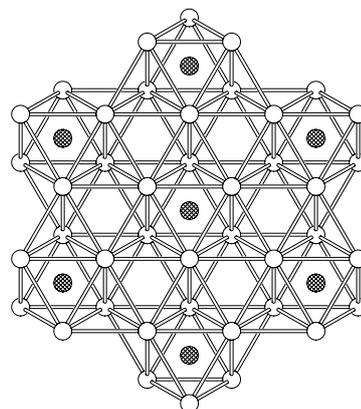


Figure 7. Typical model for fcc ($a = 3.98$ Å) virtual Tc metal 42-atomic cluster filled with 7 carbon atoms.

liquidus of graphite in the Tc-C systems.

The Tc alloy with 17.5% (at.) C in the cast and annealed at 1400 °C according to⁴ and at 1150 °C according to⁶ conditions had always a single-phase for structure of the metallic sub-lattice with the lattice periods close to 3.98(2) Å and $V/z = 15.76$ Å³ (Figure 6). This phase can be regarded as a virtual modification of cubic technetium metal stabilized with carbon or a technetium carbide with the cubic lattice of the NaCl type (δ -phase) defective in carbon.

4. Quantum Chemical Study

To analyze the stability of phases in Tc-C system the calculation was carried out by the non-empiric quantum chemistry method X_α DV using the program DVSCAT. Two cluster models with 18 and 42 metal atoms were studied (the latter presented at the Figure 7). The calculation results are given in the Tables 3 and 4. The difference of $y - y_{(0)} = (I_B(Tc_xC) - I_B(Tc_{metal}))$, where I_B – bounding index, was found to be the most sensitive parameter for the description of the cluster stability. These calculations were supported with the graphical analyses at Figure 8, where zero line corresponds to pure metal cluster, positive ΔI_B values correspond to the increase in stability relative to Tc metal, while the negative values – to the decrease in cluster stability. Although the experimental data were also approximated with a polynomial line (dotted), only qualitative sense was attributed to that dotted line without any special consideration. Both the calculations and the Figure 8 gave the evidence that:

- 1) small amounts of carbon atoms addition (1–10 at.%) result in the important increase of the cluster stability;
- 2) the tendency of decrease in Tc carbide stability with an increase of carbon content starts at least at 12% of C;
- 3) the latter tendency is not monotonic but is characterized with *sine*-type dependency, the last stable maximum being close to 17% C that corresponds to $Tc_{42}C_7$ in the frame of our model or to Tc_6C in general infinite mode. The composite with 26% C has much less probability and could doubtfully be formed as also reported at.⁶

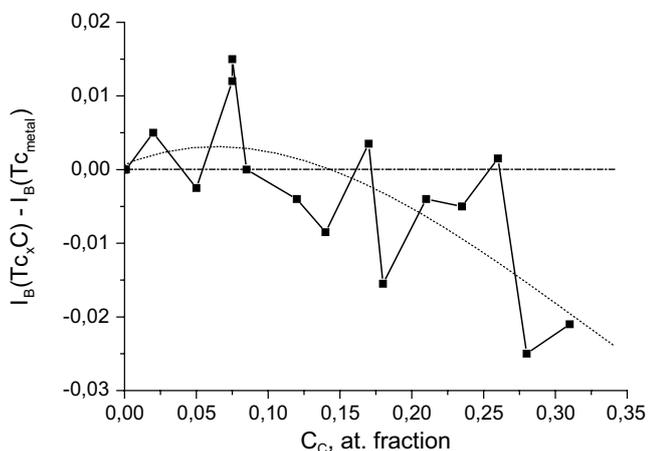
In conclusion these researches showed that technetium carbide is being formed much easier compared to previous data most probably due to the formation of newly observed intermediate orthorhombic Tc metal phase. Its formation in the spent carbide nuclear fuel became quite possible and would result in important increase in specific cell volume and hence - in the specific fuel volume.

5. Conclusions

1. A new Tc-metal phase has been found and new softer conditions for the Tc carbide formation were observed. The unit cell parameters of a new orthorhombic Tc metal were a =

TABLE 3: The Results of Quantum Chemistry Calculation by Method X_αDV Using the Program DVSCAT of the Cluster Model with 42 Metal Tc Atoms in fcc Structure (binding order per atom, carbon to technetium ratio (C/Tc), number of atoms in cluster (N_{at}), number of the bonds (N_{bond}), number of the bonds per atom (N_{bond per atom}))

Model	Number of C atoms	Binding order/atom	C/Tc	N _{at}	1/N _{at}	N _{bond}	N _{bond per atom}	N _{bond of TcTc type}	N bond TcC/TcTc	N _{electrones}
Tc42	0	1,1347	0	42	0,02381	144	3,43	144	0,00	1806
Tc42C	1	1,1402	0,0238	43	0,02326	150	3,49	144	0,04	1812
Tc42CC	2	1,1313	0,0476	44	0,02273	156	3,55	144	0,08	1818
Tc42C_C	2	1,1323	0,0476	44	0,02273	156	3,55	144	0,08	1818
Tc42C3	3	1,1497	0,0714	45	0,02222	162	3,60	144	0,13	1824
Tc42[C3]	3	1,146	0,0714	45	0,02222	162	3,60	144	0,13	1824
Tc42C4	4	1,1349	0,0952	46	0,02174	168	3,65	144	0,17	1830
Tc42C5	5	1,1301	0,119	47	0,02128	174	3,70	144	0,21	1836
Tc42C6	6	1,1254	0,1429	48	0,02083	180	3,75	144	0,25	1842
Tc42C7	7	1,1382	0,1667	49	0,0204	186	3,80	144	0,29	1848
Tc42(C7)	7	1,1327	0,1667	49	0,0204	179	3,65	137	0,31	1848
Tc42C8	8	1,119	0,1905	50	0,02	190	3,80	142	0,34	1854
Tc42C9	9	1,1255	0,2143	51	0,01961	192	3,76	138	0,39	1860
Tc42C10	10	1,1294	0,2381	52	0,01923	201	3,87	141	0,43	1866
Tc42C11	11	1,1367	0,2619	53	0,01887	201	3,79	135	0,49	1872
Tc42(C11)	11	1,1355	0,2619	53	0,01887	196	3,70	130	0,51	1872
Tc42C12	12	1,1099	0,2857	54	0,01852	207	3,83	135	0,53	1878

**Figure 8.** The $\Delta I = (I_{B(Tc_xC)} - I_{B(Tc_{metal})})$ increase in mean bond strength relative to Tc metal, attributed to 1 cluster atom in Tc carbide with variable C as a function of C content. $I_{B(Tc_xC)}$ – mean bond strength in Tc carbide, $I_{B(Tc_{metal})}$ – mean bond strength in Tc metal, C_c – Carbon concentration in the cluster in atomic fractions. Solid line: calculated data, Dash and dot line: Tc metal level, dot line: the qualitative mean tendency in the $I_{B(Tc_xC)} - I_{B(Tc_{metal})}$ index value.

2.805(4), $b = 4.958(8)$, $c = 4.474(5)\text{\AA}$ ($V/z = 15.55 \text{\AA}^3$) for Tc-C with 1.38 wt.% C and $a = 2.815(4)$, $b = 4.963(8)$, $c = 4.482(5) \text{\AA}$ ($V/z = 15.65 \text{\AA}^3$) for Tc-C with 1.96 wt.% C.

2. Quantum chemistry consideration supported the high affinity of Tc to C at low C content and also several stability regions with the last one situated at Tc/C ratio of approximately 6/1.

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TABLE 4: The Results of Quantum Chemistry Calculation by Method X_αDV Using the Program DVSCAT of the Cluster Model with 42 Metal Tc Atoms in fcc Structure, N(C)/N(Tc): The Ratio of Carbon Atoms Number to Tc Atoms Number, Mean Bond Strength in a Tc-C Cluster $y(x) = I_{B(Tc_xC)}$, $y(0)$ – mean Bond Atrength in the Pure Tc Metal Cluster

	Number of carbon atoms	X N(C)/N(Tc)	C, at.%	C, wt.%	$y(x)$	$y-y(0)$
Tc42	0	0	0	0	1,1347	0
Tc42C	1	0,02381			1,1402	0,0055
Tc42CC	2	0,047619			1,1313	-0,0034
Tc42C_C	2	0,047619			1,1323	-0,0024
Tc42C3	3	0,071429			1,1497	0,015
Tc42[C3]	3	0,071429			1,146	0,0113
Tc42C4	4	0,095238			1,1349	0,0002
Tc42C5	5	0,119048			1,1301	-0,0046
Tc42C6	6	0,142857	12.5	1.415	1,1254	-0,0093
Tc42C7	7	0,166667	14	1.98	1,1382	0,0035
Tc42C8	8	0,190476			1,119	-0,0157
Tc42C9	9	0,214286			1,1255	-0,0092
Tc42C10	10	0,238095	20	2.94	1,1294	-0,0053
Tc42C11	11	0,261905			1,1367	0,002
Tc42C12	12	0,285714			1,1099	-0,0248

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