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The Susceptibility to Hydrogen Embrittlement of Low Alloy Cr-Mo Steel Tubing

Občutljivost cevi iz nizkolegiranega Cr-Mo jekla na vodikovo krhkost

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In the paper the results of research in the susceptibility of as-rolled and heat treated low alloy Cr-Mo (microalloy by Nb) tubing to hydrogen embrittlement by method of cathodic polarization are shown. The results show that quenching at 870°C (both in water and oil) and tempering at high temperature (720°C) attain excellent resistance to hydrogen embrittlement which is indicated by a small embrittlement index (11.1–23.6%) by tough small-dimple fractures and relatively small content of absorbed hydrogen (3.2–3.4 ppm) at the cathodic polarization.
Key words: low alloy steel, tubing, hydrogen embrittlement, heat treatment, cathodic polarization

Raziskovali smo občutljivost valjanih in toplotno obdelanih cevi iz malolegiranega Cr-Mo jekla (mikrolegiranega z niobom) na vodikovo krhkost. Uporabili smo metodo katodne polarizacije. Rezultati kažejo, da s kaljenjem s temperature 870°C (v vodi ali olju) in z visokotemperaturnim popuščanjem (720°C), dosežemo odlično odpornost proti vodikovi krhkosti. Potrjuje jo majhen indeks krhkosti (11.1–23.2%), žilav, jamičasti izgled prelomne površine in relativno majhna vsebnost absorbiranega vodika (3.2–3.4 ppm) pri katodni polarizaciji.
Ključne besede: malolegirana jekla, cevi, vodikova krhkost, toplotna obdelava, katodna polarizacija.

1. Introduction

Corrosion costs of oil country tubular goods (OCTG) in oil industry are estimated to be some hundred millions dollars every year. At the begin of the fifties a lot of oil tubes in Canada, USA and France failured when API (American Petroleum Institute) pipes grade N-80 and P-110 were used in sour wells, with minimum yield strenght of 552 MPa and 758MP, respectively. Nowdays great efforts are being made to decrease or reduce the process of corrosion to minimum, expecialy the sulfide stress corrosion cracking (SSCC) i.e. hydrogen embrittlement (HE). Most producers of oil country tublar goods adapt themselvs to difficult conditions of oil and natural gas exploatation by developing and producing pipes from low alloy to high alloy steels and special alloys. Low alloyed steels mostly used for OCTG are made from medium carbon Mn, Mn-Mo and Cr-Mo type steels, microalloyed with vanadium, niobium, titan and bor[1]. The sulfide stress corrosion cracking or hydrogen embrittlement of steels is quite a complex phenomenon not being yet completely unambignous determined neither regarding the mechanism[2] nor the dominant influence of individual factors (mechanical properties, microstructure etc.). However it is often used to characterize the influences of hydrogen in steel at room temperatures. These influences are mostly manifested through the loss of ductility (decrease of reduction area and elongation). Therefore, in this paper is presented the analyse of low alloy Cr-Mo steel (microalloyed with niobium) susceptibility to hydrogen embrittlement from the point of view of mechanical properties, heat treatment and microstructure. At the same time, the content of absorpted hydrogen was determined and fractographic analysis of fractured surfaces' specimens after cathodic polarization was carried out.

2. Experimental

Material

By procedure of laboratory electro slag remelting there were received low alloy Cr-Mo steel (microalloyed with niobium) ingots, ϕ 169 x 380 mm, which were after forged into billets □ 135 x 420 mm. The **table 1** shows chemical composition of the investigated steel.

On the **table 1** we can see that the investigated steel appropriates to the first type API grade C-90 by addition of niobium as a micro alloy element[3]. Alloying with higher content of molybdenum and microalloying with niobium AISI 4130 steel proved to be useful for increasing of resistance to hydrogen cracking because of the refined austenite grain and the size of

Steel	C	Mn	P	S	Si	V	Mo	Al	Cr	Nb
Cr-Mo	0.30	0.72	0.022	0.007	0.37	0.01	0.63	0.07	1.12	0.035

Table 1: The chemical composition of steel investigated, %

Tabela 1: Kemijska sestava jekla, %

carbide particles. In Iron Steel Works Sisak, billets □ 135 x 420 mm were hot rolled into seamless tubing ϕ 60,3 x 4,83 mm for oil industry.

Heat treatment

The temperatures of phase transformations needed for heat treatment were tested by dilatometer Lk.02 "Adamel Lhomargy". The specimens ϕ 2 x 12 mm were heated and cooled by heating and cooling rate of 0,05°C/s. On registered diagram dilatation/temperature, the temperature values of particular phase transformation were read off. On the basis of there results, the heat treatment of pipes which is consisting of normalization and tempering as well as quenching (with cooling in water and oil) and tempering were carried out in the laboratory electric resistance chamber furnace. Before and after heat treatment mechanical properties of ASTM standardized specimens were tested. The hardness test was performed by Brinell's method. In a view of obtaining phase composition a phase analysis by X-ray diffraction device and Philips numerical couting technique by use CoKα radiation.

Corrosion tests

Since the hydrogen embrittlement of the material presents in fact the loss of its ductility (due to absorbed hydrogen) a decrease of ductility parameters is obvious, i.e. the reduction area and elongation of specimens are always reduced[2,4-6]. Among many electrochemical methods the cathodic polarization is one of the most appropriate methods for the determination of relative material susceptibility to hydrogen embrittlement. The specimens ϕ 3,5 x 110 mm made from steel investigated in as-rolled and heat treated state were put into electrochemical cell (fullfilled with 0,5 M H_2SO_4 + 10 mg As_2O_3/l solutin) which was put in Zwick 50 kN tensile machine and subjected to static load of 60 and 80% its of yield strenght[7]. The cathodic polarization was carried out by Wenging's potentiostat at current density of 1,6; 4,0; 8,0 and 12,0 mA/cm^2. After cathodic polarization (duration of two hours) of stressed specimens testing to the fracture with deformation rate of 2,4 x $10^{-4}s^{-1}$ was immidiately carried out. On the base of change of specimens' reduction area embrittlement index was calculated according to the following equation:

$$F = \frac{RA_{air} - RA_H}{RA_{air}} \times 100 \qquad (1)$$

where are:

RA_{air} - reduction area prior cathodic to polarization (uncharged by hydrogen)

RA_H - reduction area after cathodic polarization (charged by hydrogen)

After corrosion tests the content of absorbed hydrogen in cathodic polarized specimens is determined on the exalograph EA-1 by the method of hot extraction.

Metallographic and fractographic testing

Microstructure of polished and etched (in nital) specimens before and after heat treatment were carried out by the scanning electronic microscope (SEM) type JOEL JXA-50 A, voltage to 50 kV. For determination series and manner fracture the analysis fractured surfaces of specimens were carried out.

3. Results of investigation

Investigation of mechanical properties were carried out by Instron 1196 tensile machine on two samples in as-rolled and heat treated state. Energy impact testing was carried out by Charpy clapper on three ISO specimens with V-notch at temperature 20°C. Average testing values of mechanical properties are showed in **table 2**.

On **table 2** can be seen that the tubing without heat treatment according to mechanical properties correspond to P-110 API grade which does not belong to the corrosion resistant oil country tubular goods. By normalizing at 900°C and tempering at 700°C was obtained corrosion resistance L-80 API grade. By the tubing heat treatment consisting of quenching at 870°C and tempering at high temperature of 720°C (specimens 36 and 39) there were obtained OCTG with mechanical properties C-90 grade. The index embrittlement as per equation (1) taking into account the specimens reduction area prior and after cathodic polarization. The average values of embrittlement index for as-rolled and heat treated tubes are shown in **table 3**.

4. Discussion of results

The mechanical properties of Cr-Mo steel tubing in as-rolled state are high (API grade P-105, **table 2**) due to the chemical composition (modification with molybdenum and microalloying with niobium) and the presence of bainite microstructure (**figure**

Table 2: The mechanical properties of tubings Cr-Mo steel in as-rolled and heat treated state

Tabela 2: Mehanske lastnosti cevi iz Cr-Mo jekla v valjanem in toplotno obdelanem stanju

Specimen	Heat treatment	Yield strenght MPa	Tensile strenght MPa	Elongation %	Hardness HB	Energy impact at+20°C	Fracture toughnes MPa √M
3	–	972	1145	8.9	400	4	50
30	Normalized 900°C/min, air + Tempered 700°C/60 min, air	605	725	25.5	230	18	84
36	Quenched 870°C/30 min, water + Tempered 720°C/60 min, water	721	765	25.5	252	19	94
39	Quenched 870°C/30 min, oil + Tempered 720°C/60 min, air	703	759	22.1	250	22	100

Table 3: The values of embrittlement index and content absorbed hydrogen Cr-Mo steel by cathodic polarization

Tabela 3: Vrednost indeksa krhkosti in vsebina absorbiranega vodika Cr-Mo jekla pri katodni polarizaciji

Specimen	Heat treatment	Yield strenght MPa	Index embrittlement F (%)	Current density mA/cm²	Content hydrogen ppm
3 – 6	–	972	87.6	1.6	2.7
30 – 4	Normalized 900°C/30 min, air		27.2	4.0	
30 – 7	+	605	55.2	8.0	–
30 – 6	Tempered 700°C/60 min, air		88.5	12.8	
36 – 3	Quenched 870°C/30 min, water		11.1	4.0	3.2
36 – 5	+	721	30.7	8.0	4.0
36 – 4	Tempered 720°C/60 min, air		86.2	12.0	4.8
39 – 3	Quenched 870°C/30 min, oil		23.6	4.0	3.4
39 – 5	+	703	31.1	8.0	4.4
39 – 4	Tempered 720°C/60 min, air		88.6	12.0	7.0

3a) appearing at usual air cooling of tubes with finish rolling temperature. The hardness is homogenous through the whole cross section and amounts to 400 HB and 230-250 HB for the pipes in as-rolled and heat treated state as well. As OCTG are also used in arctic fields they are supposed to be as tough as possible, expecially at low temperatures. Energy impact of heat treated pipes is high and amounts to 18-22 J at 20°C retaining to same values also at -40°C. The fracture toughness (K_{IC}-value) is known to be an important characteristic of material, however, because of wall-thinnes (4,83 mm) K_{IC} was not defined by the way of Charpy's energy at 20°C as per Rolf-Novak's equation[8].

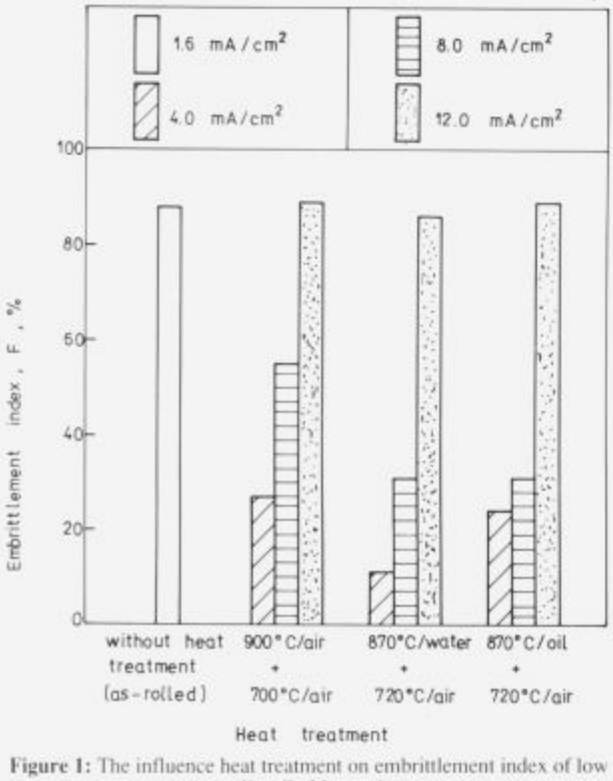

Figure 1: The influence heat treatment on embrittlement index of low alloy Cr-Mo steel

Slika 1: Vpliv toplotne obdelave na indeks krhkosti malolegiranega Cr-Mo jekla

where are: $K_{IC} = R_{eH}(0{,}646\ CVN/R_{eH} - 0{,}00635)^{1/2}$ (2)

R_{eH} - Upper yield strenght (MPa)

CVN - Charpy energy impact (J)

On the base of calculated K_{IC} - values (**table 2**) it is clear that the fracture toughness of quenched and tempered pipes has high values which may be up to 100 $MPam^{1/2}$. The **figure 1**, in the manner of histogram, shows the change of embrittlement index at the cathodic polarization both for different states of material and different current densities and it can be seen that pipes resistance to hydrogen embrittlement increases through appliance of the heat treatment, specially quenching and tempering.

Although pipe specimens in as-rolled state were at test stressed on the level of 60% yield strenght and polarized at current density of 1,6 mA/cm² a small resistance to hydrogen embrittlement with embrittlement index of 87,6% was obtained. The microfractography (**figure 2a**) of a fractured specimen made after cathodic polarization shows the presence of mixed fracture in which predominantes brittle cleavage type of fracture. The reason for such a small resistance to hydrogen embrittlement is in the presence of untempered bainite microstructure (**figure 3**) which is by many investigators[9,10] considered, after martenzite structure, to be the most unfavourable microstructure with regard to the resistance in corrosion environmetals, expecially in sulfide environmetals.

By normalization and tempering at 700°C the resistance to hydrogen embrittlement was increased can be seen from the index value of embrittlement 27,2% and from the ductile fracture with a small energy fracture (**figure 2a**). The fracture began at the large inclusion particle being however mighty traps fro hydrogen because their great intersurface encures the accummulation of sufficient hydrogen quantites for the initation of cracking[11,12]. By quenching and tempering at 720°C the tube resistance to hydrogen embrittlement was increased which was expressed by a smaller embrittlement index, particulary specimens quenched in water where the embrittlement index is only 11,1%. The fracture are ductile, with fine dimple appearence (**figure 2c**). The increase of embrittlement index was induced mosttly by presence of high tempered martenzite microstructure (**figure 3b**) in which by means of X-ray diffraction the distribution of fine sphero carbides FeC, Fe_3C, Cr_3C_2 and αMo_2C was determined. Fine carbides microstructured is a main microstructural parameter for improving of hydrogen embrittlement because in this case a longer time is needed for the accummulation of critical amount

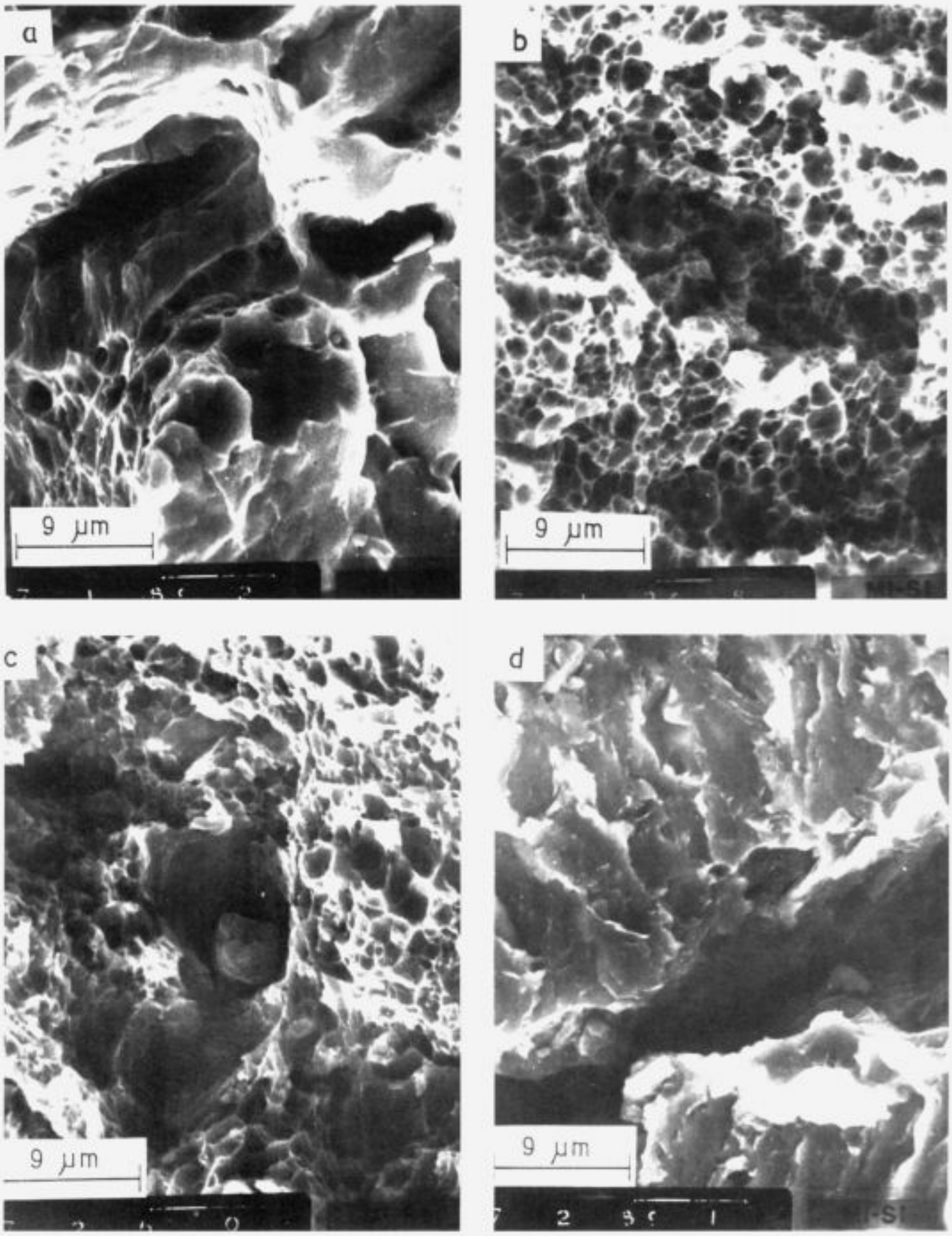

Figure 2: The microfractography of fractured surfaces of low alloy Cr-Mo steel after cathodic polarization
a) as-rolled, current density 1,6 mA/cm^2
b) quenched and tempered, current density 4,0 mA/cm^2
c) normalized and tempered, current density 4,0 mA/cm^2
d) quenched and tempered, current density 12,0 mA/cm^2

Slika 2: Mikrofraktografije prelomnih površin malolegiranega Cr-Mo jekla po katodni polarizaciji
a) valjano, gostota toka 1,6 mA/cm^2
b) kaljeno in popuščeno, gostota toka 4,0 mA/cm^2
c) normalizirani in popuščeno, gostota toka 4,0 mA/cm^2
d) kaljeno in popuščeno, gostota toka 12,0 mA/cm^2

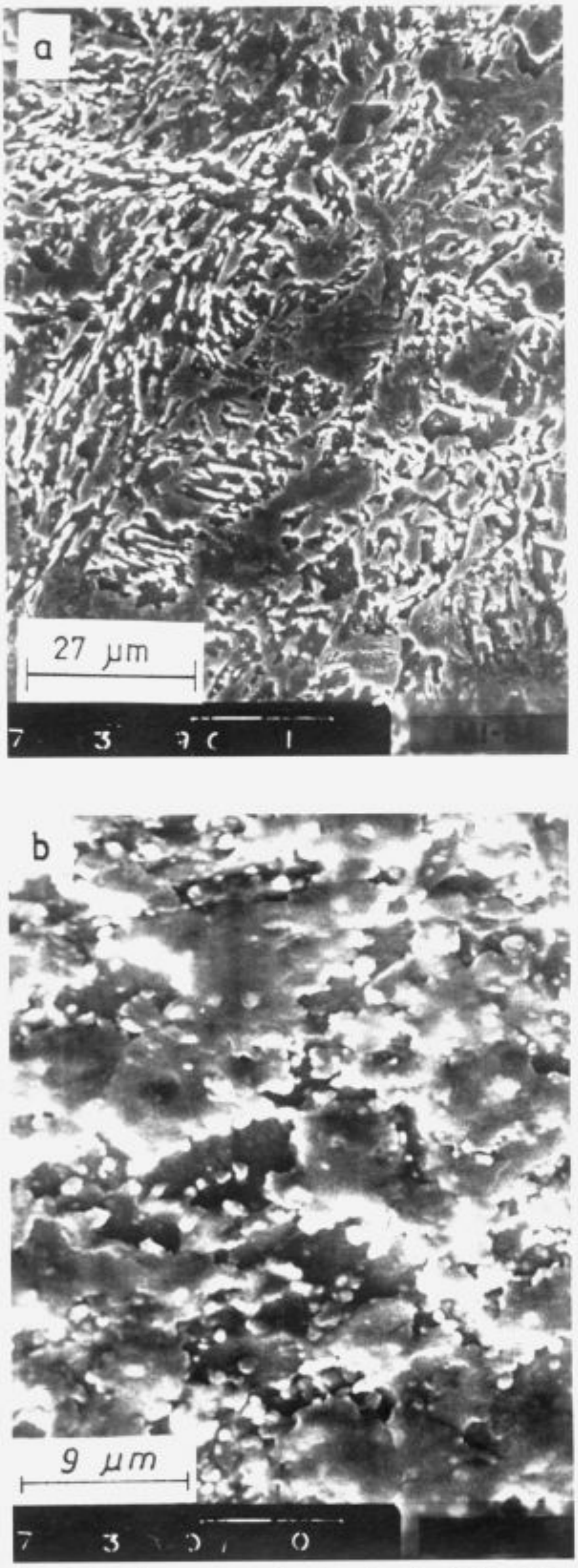

Figure 3: The microstructures tubings from low alloy Cr-Mo steel in as-rolled (a) and quenched and tempered state (b)

Slika 3: Mikrostruktura cevi iz malolegiranega Cr-Mo jekla v valjanem (a) ter kaljenem in popuščanem stanju (b)

of hydrogen inducing the brittle material decay. Since the microstructure influence is manifested mainly through the absorption and trapping of hydrogen on the interfaces carbide/matrix, the defined fine chrome carbides Cr_3C_2 and αMo_2C increase resistance to hydrogen embrittlement.

5. Conclusion

The tubing of investigated Cr-Mo steel in as-rolled state (without heat treatment) in regard to mechanical properties correspond to API grade P-110 with bainite microstructure appeared in usual way by air cooling of pipes at finished rolling temperature. Their resistance to hydrogen embrittlement is small with high values of embrittlement index of 87,6%. It proves also the presence of mixed fracture with mainly brittle cleavage fractures. By normalizing of tubing at 900°C and tempering at 700°C is obtained API grade L-80 with a great resistance to hydrogen embrittlement (F = 27,8%) and ductile fracture with a small fracture energy. However, by quenching and tempering at 720°C API grade was obtained C-95 with significant resistance to hydrogen with ductile mainly fine dimple fractures. The reason of there are carbides Cr_3C_2 and αMo_2C in tempered martenzite microstructure. However, by increasing of current density from 4,0 mA/cm^2 to 12,0 mA/cm^2 at cathodic polarization some quintity of hydrogen (5-7 ppm) was absorbed which remarkably decreased resistance to hydrogen embrittlement (F = 86-89%) in the presence of the brittle cleavage transgranular fracture. The results of the test show that for the obtaing of API grade C-95 with high resistance to hydrogen embrittlement the heat treatment of tubing from investigated Cr-Mo steel needs to be carried out by quenching in water after having reached the temperature at 870°C and air tempering from 720°C.

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