

# The effects of auto-tempering martensite on mechanical strength of a microalloyed steel containing boron and titanium

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## Abstract

Oil Country Tubular Goods (OCTG) steels are used in the form of tubes in the casing column of the oil well walls and exhibit tempered martensitic structure after quenching and tempering. In these steels, due to the high cost of chromium, nickel and molybdenum, an alternative is the replacement of these elements by boron, which increases the hardenability. In order to maintain the efficiency of boron in solution during the quenching, it is necessary to add titanium to form titanium nitrides (TiN), which inhibit austenitic grain growth and avoid the formation of boron nitride. Another factor is to evaluate the effect of heat treatment on the mechanical properties of this steel. In the present study were evaluated the microstructure, hardness and tensile properties of a microalloyed hot rolled steel containing boron and titanium after heat treatments. Samples of a coil were quenched at 850 and 1050°C and then tempered at 200 and 600°C. The results show that the hardness, yield stress and tensile strength after austenitization temperature at 1050°C are smaller, due to the formation of auto-tempering martensite in the quenching.

**Keywords:** Boron steels; Titanium nitride; Auto-tempering martensite; Hardenability.

## 1 Introduction

OCTG steels are used in the manufacture of tubes to be applied as columns in the oil wells. The steels used in these columns must provide compatible hardness with the tensile properties, as well as corrosion and abrasion resistance, with the minimum wall thickness.

The heat treatment are responsible for meeting the requirements of API SPECT 5CT standard and is closely associated with the transformation and morphology of martensite. According to the literature, the martensite transformation accompanied with auto-tempering would occur at the coiling temperature, because the residual heat is difficult to transfer into surroundings [1]. In this case, the softening of martensite after auto-tempering is associated with the migration of carbon atoms, precipitation of particles and recovery of dislocation structure [2]. However, many researches also demonstrated, that carbon and nitrogen could segregate, pin the dislocations and increase mechanical properties, when the tempering temperature increased to  $\pm 250^\circ\text{C}$  [3,4].

Another important factor in the quality of OCTG steels is the chemical composition. Due to the high cost of chromium, nickel and molybdenum, boron is added as an

alternative chemical element to increase the hardness, yield strength and tensile strength. Boron is an interstitial element with low solubility in ferrite and is added in the range of 10 to 30 ppm in steel. Boron segregates in grain boundaries, inhibits the ferritic nucleation and favors the martensitic transformation [5]. In order to maintain the efficiency of boron in solid solution it is necessary to add titanium to stabilize nitrogen by forming titanium nitride (TiN), instead of boron nitride. Titanium nitride hinders grain growth at soaking temperatures [6]. In this context, the objective of this research was to evaluate the effects of coiling temperatures at 200 and 600°C on the mechanical properties of one oil country tubular goods steel, considering the formation of auto-tempering martensite. To simulate the coiling temperatures, samples of the plates were subjected to heat treatments of quenching and tempering at different temperatures. The effect of nitrogen and boron was observed by microstructural characterization after quenching and tempering at different temperatures. The austenitization temperatures, close to and above  $A_{c3}$ , were chosen to evaluate the effect of titanium nitride on grain size.

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## 2 Materials and methods

The steel was prepared in a converter and continuous casting into slabs of 6.0x1.5x0.2 m. The slabs were heated up to 1200 °C and were continuously hot rolled into a thickness of 7.5 mm. Twelve samples of 300x35x7.5 mm were cut from one of these plates in the longitudinal direction of rolling. Six samples were heated in an electric furnace at 850°C for 30 minutes and then water quenched. Further, three of them were tempered at 200°C and three at 600°C for 50 minutes. The other six samples were heated at 1050°C for 30 minutes and then water quenched. The tempering was similar to that of quenched at 850°C. After quenching and tempering, the samples were cooled in water at 23 °C and the cooling rate was controlled in the range of 10 to 50°C per minute. In this research, two different austenitization temperatures were used to evaluate the effect of titanium nitride on the size of the austenitic grain. Regarding tempering temperatures, they can be controlled in the coiling, after rolling, to obtain different mechanical properties in steel. Afterward, specimens as ASTM E8/E8M, were submitted to tensile tests in an universal hydraulic test machine with a capacity of 500 kN and strain gauge with measurable deformation of 50 mm.

Three specimens in each condition were pulled with 1 mm per minute constant speed. To reveal the microstructure the tensile tests specimens were prepared according to conventional metallographic methods and were immersed in 2% Nital reagent (2% nitric acid in ethyl alcohol) for approximately 30 seconds. Lepera reagent (1% sodium metabisulfide in water plus 4% picric acid in ethyl alcohol) was prepared to reveal the auto-tempering martensite and ferric chloride reagent (5g FeCl<sub>3</sub>, 50 ml HCl and 100 ml H<sub>2</sub>O) to evaluate the austenitic grain size.

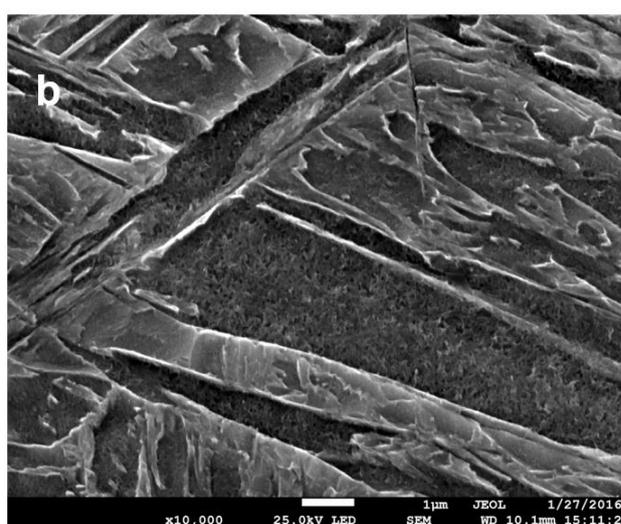
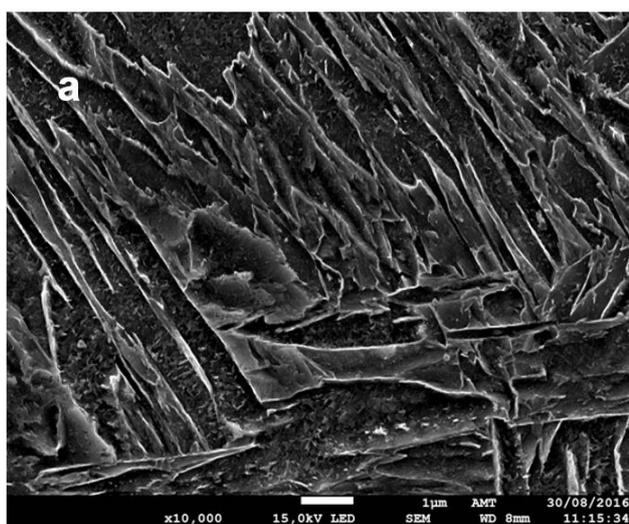
The microstructures were characterized by Scanning Electronic Microscope (SEM) with Energy Dispersive Spectrometry (EDS) system. The hardness of the matrix and phases were measured by Vickers hardness with load of 10 kgf and Vickers microhardness with load of 50 gf considering the ISO 6507-1 standard. Results represent the average of five measurements in each specimen after quenching and tempering. The austenitic grain sizes were measured according to ASTM E112.

## 3 Results

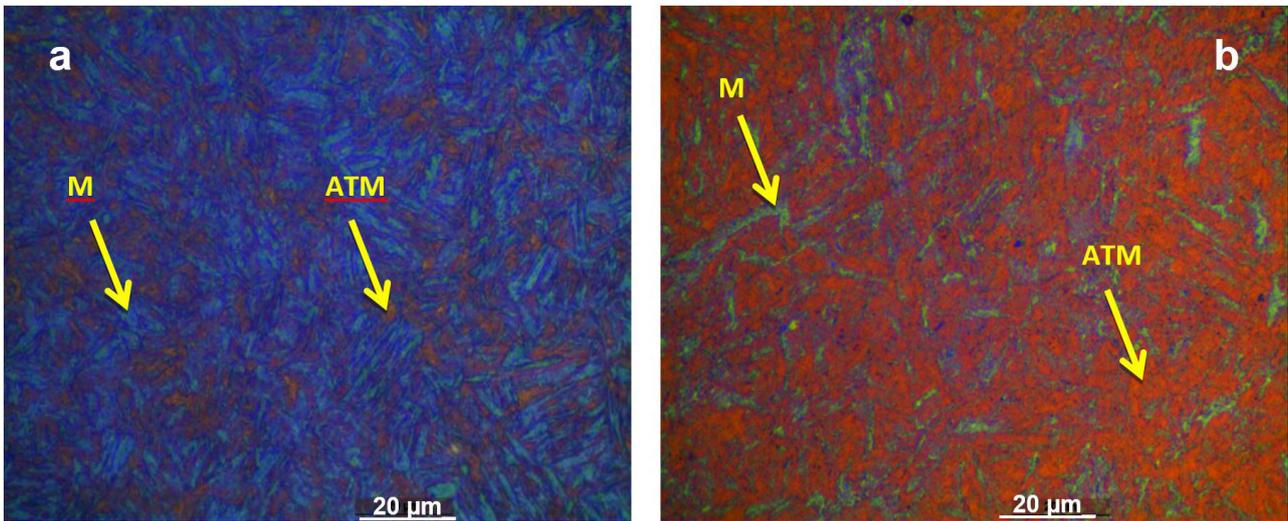
Table 1 shows the chemical composition of the microalloyed steel. Figures 1a and 1b show the microstructures of martensite laths after quenching at 850 and at 1050°C, respectively. Figures 2a and 2b, after quenching at 850 and at 1050°C, show the martensite laths (blue color) and auto-tempering martensite (brown color). Figures 3a and 3b show the microstructures after quenching at 850 and 1050°C and tempering at 200°C, respectively. Figures 4a and 4b show coalesced carbides in the steel after quenching at 850 and 1050°C and tempering at 600°C [7]. Table 2 and Figures 5a and 5b show the austenitic grain size, after quenching at 850 and 1050°C. Figure 6a shows the eutectic titanium nitride and Figure 6b the EDS spectrum. Table 2 and Figures 5a and 5b show the austenitic grain size, after quenching at 850 and 1050°C. Table 3 shows the averages of five Vickers microhardness measurements of martensite and auto-tempering martensite in the steel, after quenching at different temperatures. Table 4 presents the average of five values of Vickers hardness, yield strength ( $\sigma_y$ ), tensile strength ( $\sigma_{max}$ ) and elongation, after quenching and tempering at different temperatures.

**Table 1.** Chemical composition of the microalloyed steel (% in weight)

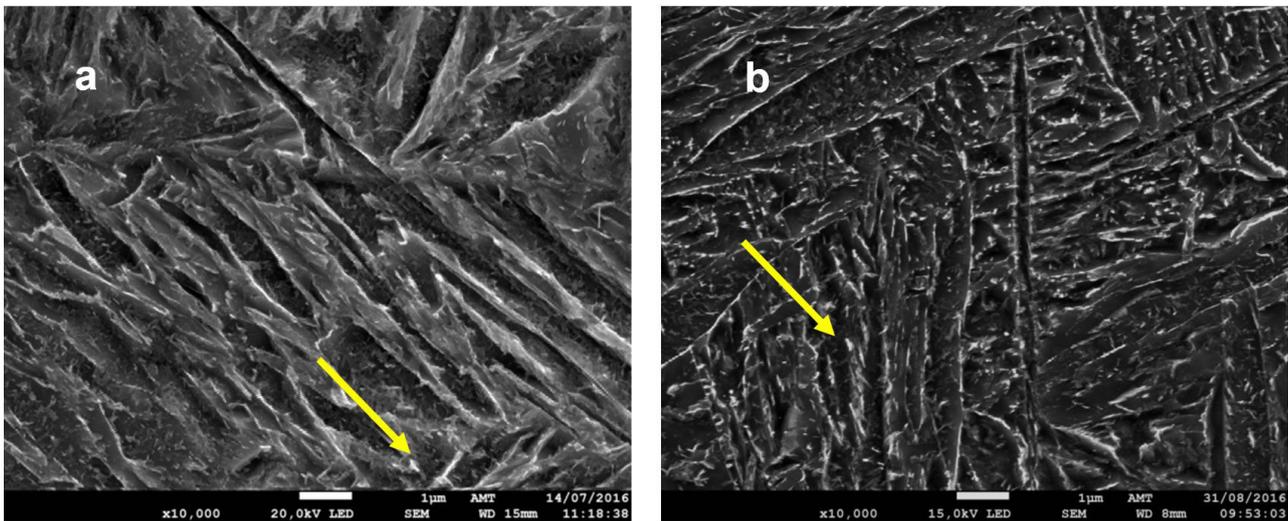
C	Mn	Si	P	S	Ti	N	B	Fe
0.23	1.26	0.24	0.013	0.0018	0.019	0.005	0.0013	Balance



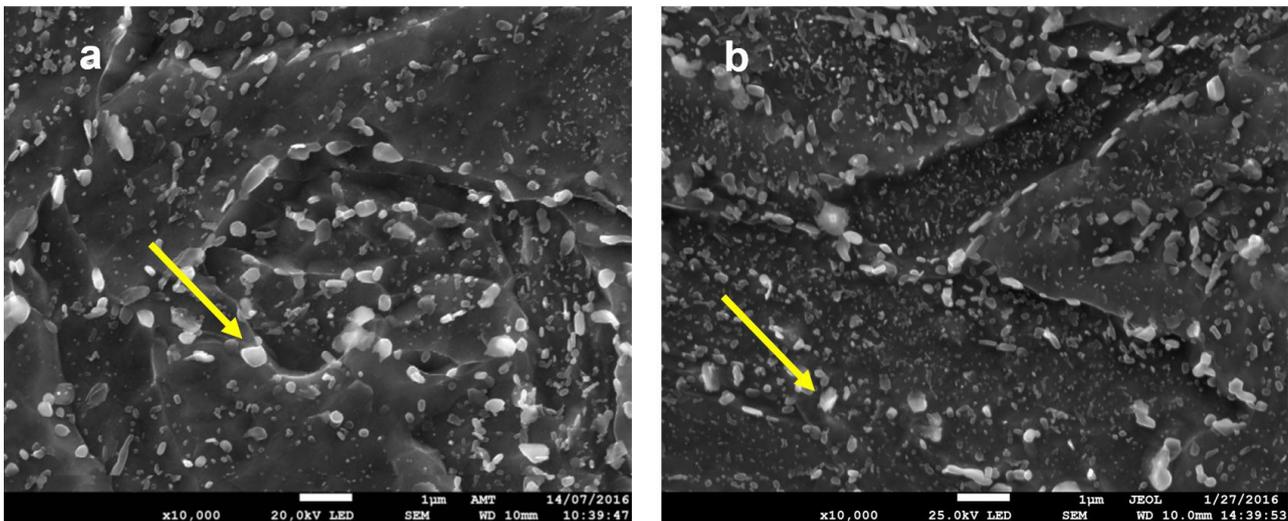
**Figures 1.** (a) and (b) Martensite laths after quenching at 850°C and 1050°C (2% Nital, SEM).



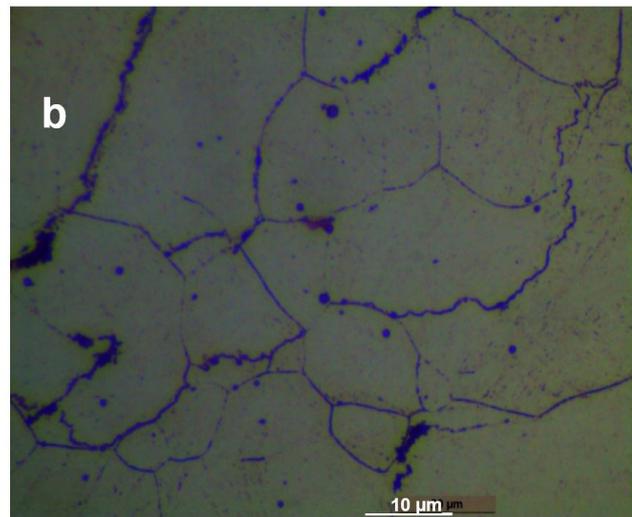
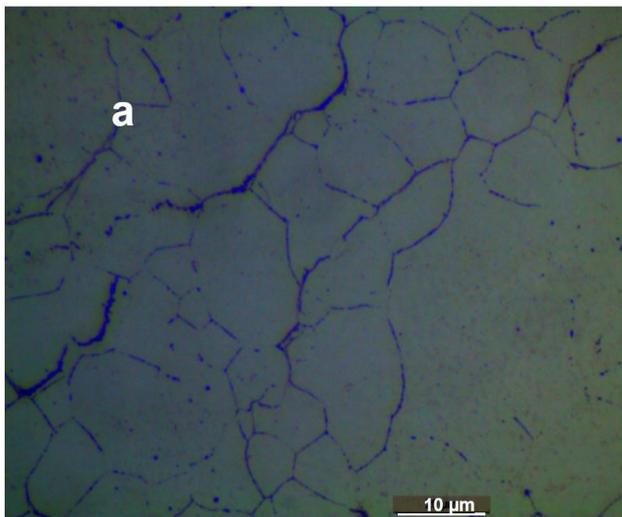
Figures 2. (a) and (b) Blue regions of martensite laths (M) and brown regions of auto-tempering martensite (ATM). Quenching at 850°C and 1050°C (Lepera, OM).



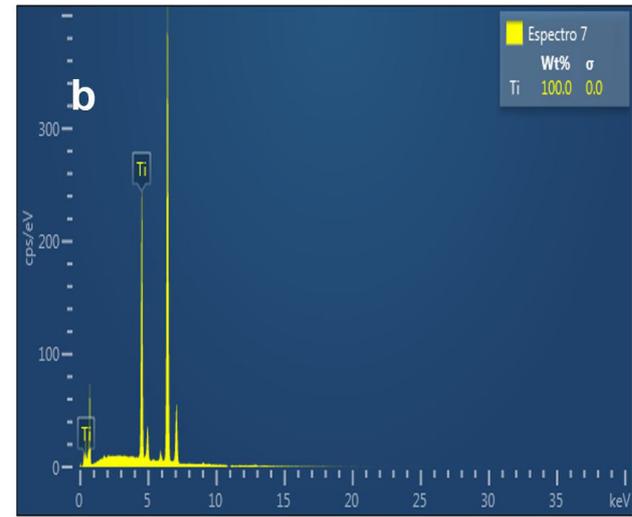
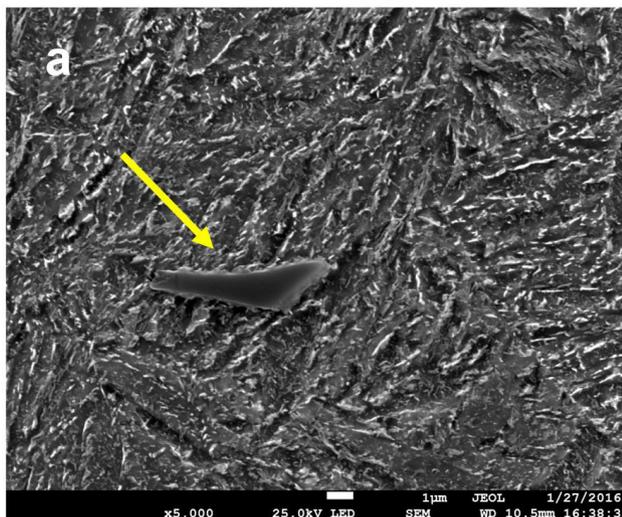
Figures 3. (a) and (b) Tempered martensite and carbides precipitation in the matrix after quenching at 850°C plus tempering at 200°C and quenching at 1050°C plus tempering at 200°C (2% Nital, SEM).



Figures 4. (a) and (b) Tempered martensite with coalesced carbides in the matrix after quenching at 850°C plus tempering at 600°C and quenching at 1050°C plus tempering at 600°C (2% Nital, SEM).



**Figures 5.** (a) and (b) Austenitic grain size after quenching at 850°C and 1050°C (Ferric chloride-MO).



**Figure 6.** (a) and (b) Morphological characteristic of titanium nitride and the EDS spectrum (2% Nital, SEM).

**Table 2.** The austenitic grain size after quenching at different temperatures according ASTM E112

Temperature	Grain Size (ASTM)	μm
850°C	7.0 ± 0.5	32 ± 1
1050°C	8.0 ± 0.5	23 ± 2

**Table 3.** Vickers microhardness of martensite and auto-tempering martensite (AT Martensite)

Quenching	Martensite (HV)	AT Martensite (HV)
850°C	504 ± 10	439 ± 10
1050°C	493 ± 10	430 ± 15

#### 4 Discussion

The N/Ti ratio of 3.8, in the chemical composition in Table 1, indicates that all nitrogen is bound to titanium. So boron is free in solid solution to be effective to form martensite laths after quenching [5,8]. The microstructures of martensite laths

**Table 4.** Vickers hardness, yield strength ( $\sigma_y$ ), tensile strength ( $\sigma_{max}$ ) and elongation after quenching (Q) and quenching plus tempering (Q+T) of steel

	Temperature	Q	Q+T 200°C	Q+T 600°C
Hardness (HV)	850°C	400 ± 10	440 ± 11	213 ± 5
	1050°C	344 ± 5	359 ± 6	201 ± 4
$\sigma_e$ (MPa)	850°C	1018 ± 10	1198 ± 11	517 ± 7
	1050°C	934 ± 9	1113 ± 13	489 ± 5
$\sigma_{max}$ (MPa)	850°C	1509 ± 13	1449 ± 12	624 ± 7
	1050°C	1382 ± 12	1376 ± 11	612 ± 6
Elongation (%)	850°C	10 ± 1	12 ± 2	27 ± 3
	1050°C	12 ± 2	12 ± 1	27 ± 3

is favored by quenching temperatures above 800°C in boron steels [9]. In this case, the temperature  $A_{c3}$  is approximately 780°C, according to the Kasatkin equation [10]. Regarding the Vickers hardness it is possible to observe in Table 4, after quenching and quenching plus tempering, that the values at 1050 are less than 850°C. This can be explained by the

larger grain size and the greater amount of auto-tempering martensite after quenching at 1050°C. The auto-tempering microstructure is associated with the migration of carbon and carbide precipitation at the martensite, and according to the literature, improves the plasticity of the steel [6]. The characterization was possible with Lepera reagent attack that shows the initial martensite (blue color) and the auto-tempering martensite (brown color), besides microhardness measurements in these regions. It can be seen at 1050°C a greater amount of auto-tempering martensite formed in the cooling to room temperature. It is likely, that the solubility of carbon in austenite favors the higher amount of auto-tempering martensite [1]. The values in Table 3 confirm the microhardness differences between martensites after quenching, due to the *c/a* variation of the body centered tetragonal structure [11,12]. In steels with more than 0.2% carbon, after tempering in the range of 100 to 250°C, it is possible that transition carbides less than 100 angstrom precipitate from martensite and hinder the dislocations movement. These constituents nuclei and grow faster than cementite [13,14]. Although, other researchers connect this mechanism to the nitrogen and carbon interstitials, both cases explain the increase in the hardness and yield stress values shown in Table 4 [3,4].

With regard to the temperature at 600°C, the carbides coalesce (Figures 4a and 4b) and favors the decrease of hardness, the yield strength and the tensile strength, but increases elongation, as shown in Table 4 [7,12]. Unlike Figures 3a and 3b with a small amount of cementite, the microstructure presents an aggregate of tempered martensite with a large number of spheroidal iron carbides. According to Table 4, coalescence is likely to be more important than differences in austenitic grain and martensite packet size. With relation

to the austenitic grain sizes, the values, after quenching at 850 and 1050°C, are in the range of seven to eight ASTM as shown in Table 2 and Figures 5a and 5b [15-17]. It is possible that titanium nitrides promote the refining of the austenitic grain during rolling at 1200°C and after quenching at 850 and 1050°C the values are similar [18]. Then it will be possible to obtain different mechanical properties with a lower austenitization temperature and, therefore, reduce the cost of heat treatment. In addition, tempering temperatures can be controlled in the coiling. Figure 6a shows the eutectic titanium nitride. The EDS spectrum in Figures 6b confirms the chemical composition of the precipitate.

## 5 Conclusions

- After quenching, auto-tempering martensite associated with austenite grain and martensite packet sizes, promotes the values reduction of hardness, yield strength and tensile strength of the steel;
- Lepera reagent and Vickers microhardness measurements allows the identification of auto-tempering martensite;
- Titanium nitride inhibits the austenitic grain growth and the values are similar after austenitization in the range of 850 to 1050°C.

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