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Study of Aluminum Nitride Precipitation in Fe- 3%Si Steel

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For good performance of electrical steels it is necessary a high magnetic induction and a low power loss when submitted to cyclic magnetization. A fine dispersion of precipitates is a key requirement in the manufacturing process of Fe- 3%Si grain oriented electrical steel. In the production of high permeability grain oriented steel precipitate particles of copper and manganese sulphides and aluminium nitride delay normal grain growth during primary recrystallization, causing preferential growth of grains with Goss orientation during secondary recrystallization. The sulphides precipitate during the hot rolling process. The aluminium nitride particles are formed during hot rolling and the hot band annealing process. In this work AlN precipitation during hot deformation of a high permeability grain oriented 3%Si steel is examined. In the study, transfer bar samples were submitted to controlled heating, compression and cooling treatments in order to simulate a reversible hot rolling finishing. The samples were analyzed using the transmission electron microscope (TEM) in order to identify the precipitates and characterize size distribution. Precipitate extraction by dissolution method and analyses by inductively coupled plasma optical emission spectrometry (ICP-OES) were used to quantify the precipitation. The results allowed to describe the precipitation kinetics by a precipitation-time-temperature (PTT) diagram for AlN formation during hot rolling.

Keywords: *silicon steel, precipitation, aluminum nitride*

1. Introduction

Electrical steels are used in electric power applications, typically as magnetic core materials for transformers, electric motors and generators. The sharp texture in grain-oriented electrical steels is developed through secondary recrystallization. A basic metallurgical principle of secondary recrystallization is the inhibition of normal grain growth by the second phase particles present during primary recrystallization[1].

It is well known that manganese sulfide (MnS), copper sulphide (CuS) and aluminum nitride (AlN) have been extensively used as grain growth "inhibitors" in electrical steels. The morphology, volume fraction and particle size distribution of precipitates have considerable importance in improving the final texture and, therefore, the magnetic properties of grain oriented steels. As large particles only exhibit a very small pinning effect on grain boundaries, it is important to know how to produce a fine dispersion of precipitates during hot rolling and first annealing. Thus, detailed and clear description of precipitation at high temperatures is of great interest[2].

The most crucial point in manufacturing grain oriented silicon steel with high permeability, using AlN as the inherent inhibitor is to ensure that the AIN is finely precipitated in the processes from steel making through hot-rolled sheet annealing.

The solubility product of AlN in silicon-steel, both in ferrite[4] and austenite[3], have been described in literature and are expressed by Equations 1 and 2, respectively:

$$Ferrite \Rightarrow \log\left[(\%Al)(\%N)\right] = -\frac{8296}{T} + 1.69 \quad (1)$$

$$Austenite \Rightarrow \log\left[(\%Al)(\%N)\right] = -\frac{7400}{T} + 1.95 \quad (2)$$

Precipitation of AlN in silicon steel has been studied by Iwayama and Haratani[5] and by Oh[6]. In this work the precipitates formed during hot deformation were characterized and the AlN precipitation kinetics was investigated. The results are discussed and compared to those obtained by Iwayama and Haratani[5] and Oh et al.[6].

2. Experimental Procedure

Transfer bar samples of Fe- 3%Si Steel, which chemical composition is shown in Table 1, were used to prepare compression specimens with 90 mm in height and 10 mm in diameter. The specimens were initially heated to 1370 °C

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for 30 minutes and rapidly cooled in cold water. To prevent oxidation during heating and soaking the samples were sealed in quartz tubes under vacuum. Compression tests were carried out in a Gleeble 3500 machine using Strain Induced Crack Opening (SICO) Testing as schematically shown in Figure 1. The tests were designed to study precipitation under conditions that simulate a reversible hot rolling finishing: the specimens were heated in the Gleeble machine to 1350 °C for 5 minutes, cooled at 25°C/s to the test temperature (1200 °C, 1100 °C, 1000 °C and 900 °C), held for 3s for equalization before the first deformation pass; deformation of 40% was applied at a rate of $0.13s^{-1}$, followed by soaking at the test temperature for different soaking times (1, 10, 100, 1000s) before the second deformation of 40% was applied, at the same deformation rate, followed by fast cooling in water.

In order to characterize the precipitates formed during the thermo-mechanical treatments, high resolution transmission electron microscopy observations were performed on carbon extraction replicas. Samples were prepared using standard techniques. To quantify the precipitation of AlN, the sample was dissolved with a solution of I_2 in methanol. The solution was filtered and the residual, collected on a filter, was dissolved in a HCl solution and filtered again. The solution, added to HNO_3 to destroy any organic trace, was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). The intensity of the emitted light from AlN was measured.

3. Results and Discussion

For all test conditions the precipitate particles were identified by EDS analysis and selected area diffraction. For each kind of particle, sulphide, nitride or co-precipitate of sulphide and nitride, the particle size distribution was obtained from around 200 particles analysed per sample.

Table 1. Chemical composition of the sample.

Element	Si	C	N	Al	Cu
%At	3,028	0,069	0,0094	0,0216	0,0941

Figure 2 Shows the extraction replica micrograph and EDS spectrum of a sample deformed at 900 °C, 1000 °C, 1100 °C and 1200 °C with 1000 s holding time between deformations. There are particles with spherical morphology and particles with spherical morphology associated with a cubic morphology. The particles with spherical morphology were identified as copper sulphide (Cu_xS) precipitates and the particles with spherical morphology associated with a cubic morphology were identified as Cu_xS+AlN precipitates, where the spherical part corresponds to the Cu_xS and the cubic morphology to AlN. It is possible to observe also a difference in contrast between Cu_xS and AlN precipitates: Cu_xS shows darker contrast with the carbon layer whereas AlN contrast is weak. At 900 °C similar precipitates were observed even at 1s soaking time between deformations, showing that under the test conditions of the present work incubation time for AlN precipitation at 900 °C is below 1s. The frequency of Cu_xS+AlN particles increased with soaking time and the average particle size was 50 nm.

Selected area diffraction has shown that the Cu_xS particles are hexagonal close-packed with lattice parameters a = 0.3794 nm and c = 1.6341 nm; and that the AlN particles are face centred cubic crystals with lattice parameter a = 0.3956 nm, see Figure 3.

At 1000 °C test temperature the spherical particles were identified as Cu_xS and (Cu,Mn)S. The latter tended to increase in frequency with soaking time. The AlN precipitates appear associated with Cu_xS, as described before, and with (Cu,Mn)S. Nitride precipitates, associated with sulphides, were observed even at 1s soaking time, but the frequency of such precipitates increased with soaking, particularly above 100s soaking. Average AlN co-precipitate particle size increased with soaking time, from 39 nm at 1s soak to 73 nm at 1000s soak.

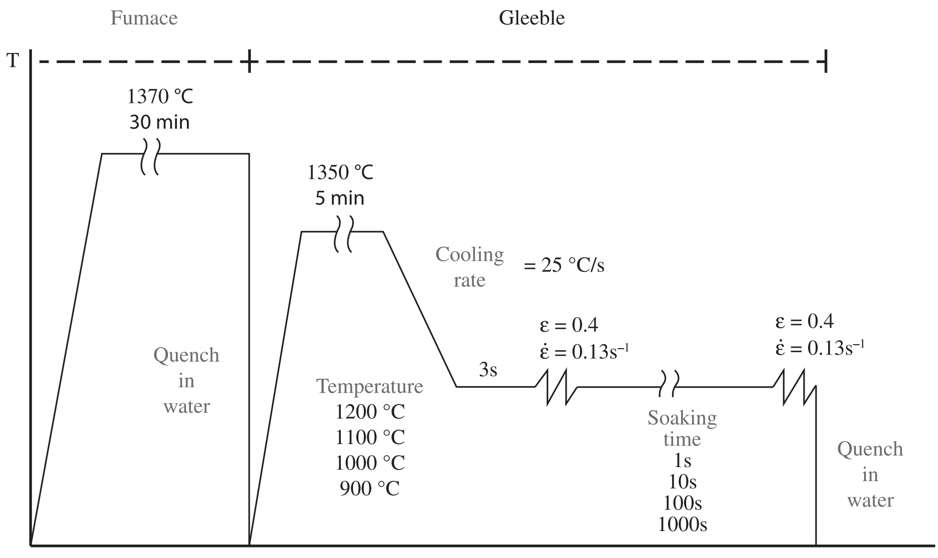
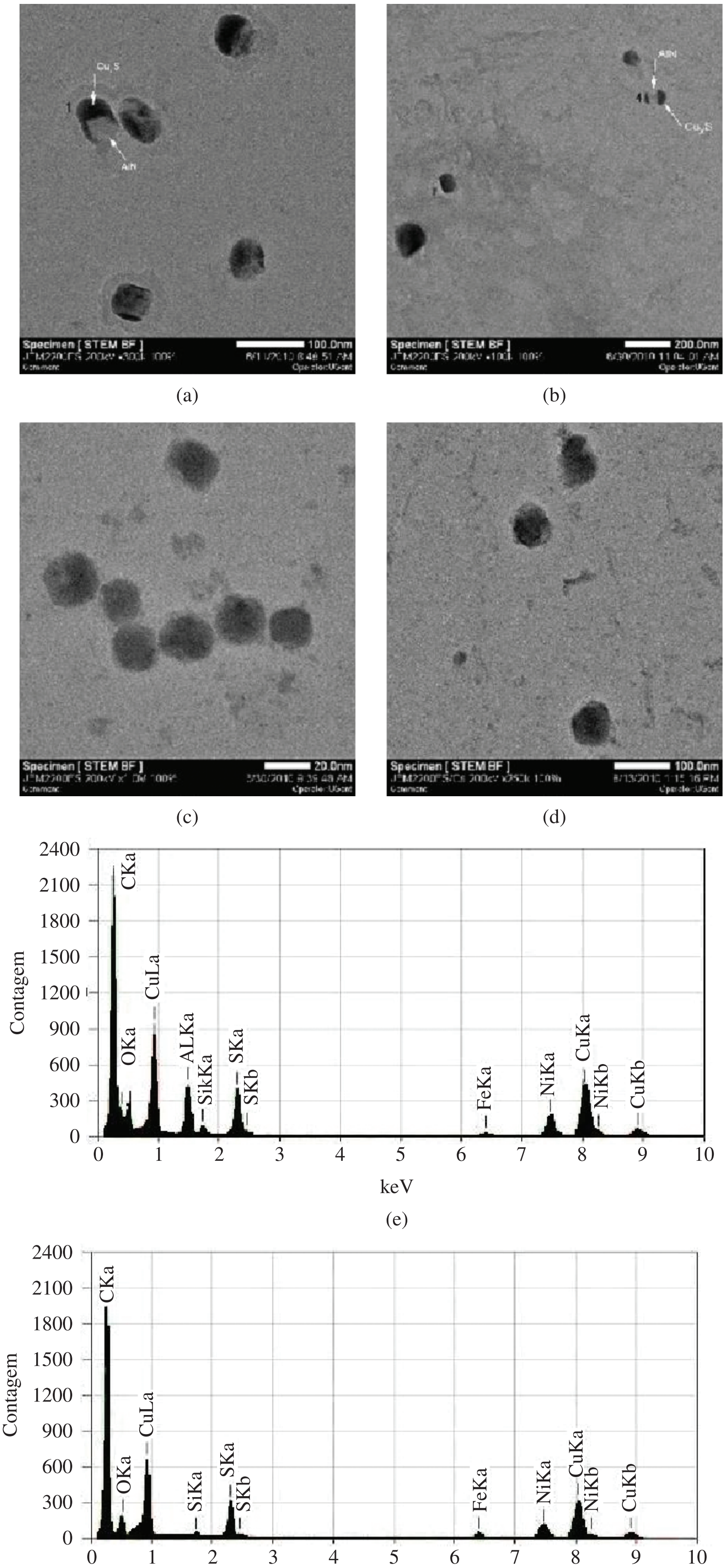


Figure 1. Annealing curve and thermomechanical treatment schedule for compression testing.



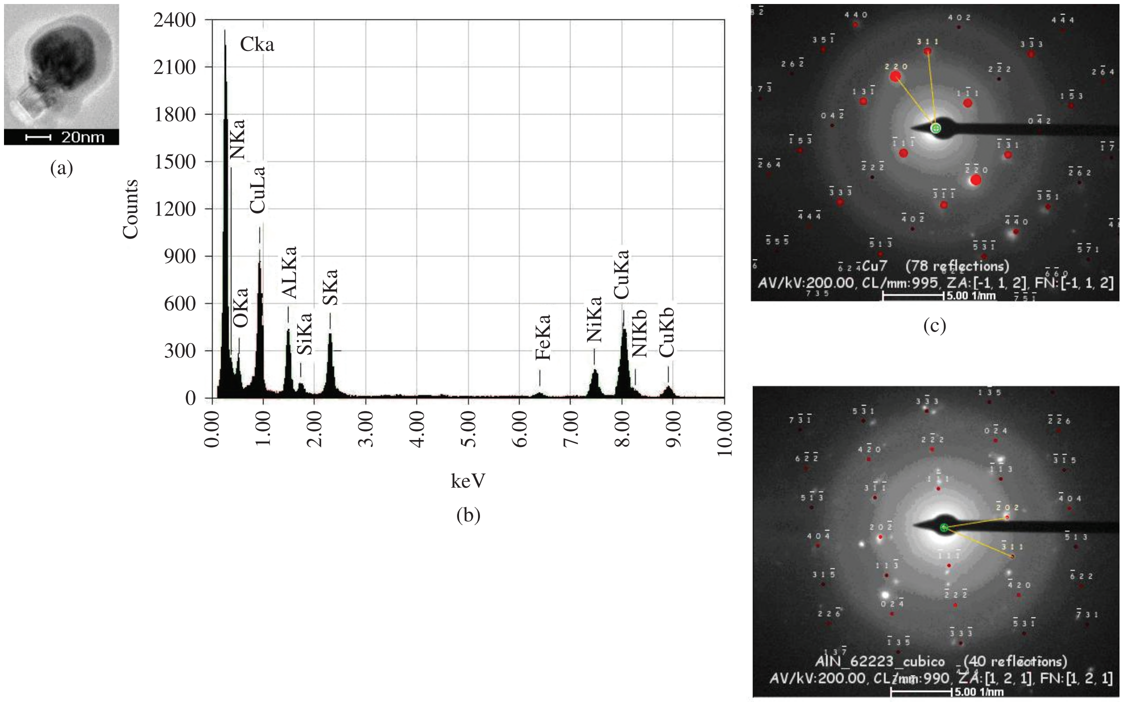
(a) (b)

(c) (d)

(e)

(f)

Figure 2. TEM carbon extraction replica micrograph showing precipitation of Cu$_x$S+AlN and Cu$_x$S at 900°C (a), 1000°C (b), 1100°C (c) and 1200°C (d), and EDS spectrum of the Cu$_x$S+AlN particles (e) and Cu$_x$S (f) with 1000 s holding time between deformations.



(a) (b) (c) (d)

Figure 3. Micrograph of Cu_xS+AlN precipitate (a), EDS spectrum (b) and diffraction pattern ((c) and (d)) for the sample performed at 900°C.

By selected area diffraction two kinds of copper sulphides were identified: Hexagonal close-packed as described above, and face centred cubic with lattice parameter a = 0.5582 nm. Based on average EDS results the face centred cubic particles could be described as $Cu_{1.8}S$. The (Cu,Mn)S precipitates also showed face centred cubic structure with lattice parameter a = 0.559 nm.

For the test temperatures of 1100 °C and 1200 °C the precipitate particles were predominantly sulphides, with increasing frequency of (Cu,Mn)S particles with increasing temperature and soaking time.

On the aluminum nitride formation, Al + N = AlN, the stoichiometry relation between nitrogen (N_P) and aluminum (Al_P) contents on the precipitate formation is given by Equation 3:

$$Al_p = \frac{26.98}{14.01} N_p \tag{3}$$

The contents of Al and N dissolved in each phase, in a specific temperature, were obtained by the difference related to Al and N totals in the steel, Al_T and N_T, respectively Equation 4 and Equation 5:

$$Al_d = Al_T - Al_P \tag{4}$$

$$N_d = N_T - N_P \tag{5}$$

According to the Equation 1 and 2, the solubility product of aluminum nitride in each phase is given by Equation 6:

$$L_{AlN} = 10^{\left(-\frac{A}{T}+B\right)} \tag{6}$$

That is, $Al_d N_d = L_{AlN}$, which enables to obtain the following Equation 7 to calculate the precipitated nitrogen content in a phase, according to temperature.

$$\frac{26.98}{14.01} N_P^2 - \left(Al_T + \frac{26.98}{14.01} N_T \right) N_P - 10^{\left(-\frac{A}{T}+B\right)} + Al_T N_T = 0 \tag{7}$$

The value of N_d obtained represents the solubility limit on the considerer phase. With the austenite and ferrite fractions given by Thermo-Calc and the expressions of aluminum nitride solubility product on the austenite and ferrite, Equation 1 and Equation 2, it is possible to calculate the contents of N dissolved on the steel according to the temperature $\left(N_d^{steel}\right)$ by the Equation 8:

$$N_d^{steel} = N_d^{\alpha} f_{\alpha} + N_d^{\gamma} f_y \tag{8}$$

Where f_α and f_γ are the equilibrium fraction of ferrite and austenite and, N_d^{α} and N_d^{γ} are the limits of solubility on the respective phases. As the stoichiometry relation on the precipitate is kept, you can obtain the values of N and Al precipitated on the steel according to temperature.

The amount of Al as precipitate, measured by dissolution and ICP-OES analysis, for the different test temperatures and soaking times, is shown in Figure 4. To estimate the fraction of precipitation for the different test temperatures and soaking times, in relation to the equilibrium, it was assumed that Al in the precipitates is present only in AlN particles. The amount of Al as AlN in the equilibrium was calculated from Equations 1 and 2 and of the equilibrium percentages of ferrite and austenite at the different temperatures. The equilibrium percentage of

Al as AlN precipitate, as a function of temperature, is also shown in Figure 4. For high test temperatures and long soaking times the values of Al as AlN tend to approach the calculated equilibrium values. According to Figure 4, AlN precipitation starts at 1124 °C.

Figure 5 shows the PPT curve for aluminum nitride obtained in this work, showing precipitation start and 50% precipitation, compared with start precipitation obtained by Haratani[5] and by Oh[6]. In order to elaborate this curve it was calculated the ratio between the values of Al as AlN precipitate found by ICP-OES analyses and the values of Alp calculated as described earlier. The shortest precipitation time in Haratani's work was 14s at 1150 °C; in Oh's work, 95s at 1000 °C; in the present work, less than 1s at a temperature lower than 900 °C.

For a temperature of 900 °C, the high dislocation density produced with the initial deformation and the lower recuperation rate propitiates a higher nucleation rate, hence the higher fraction precipitated for permanence time of 1s and 10s. As the growth rate of particles is lower than 1000 °C, because of the lower diffusion coefficient, and the volumetric fraction of precipitate on the equilibrium is higher (900 °C), for long permanency time the percentage precipitated is lower than 1000 °C. Also, for a long time of permanence at 900 °C, the recuperation will lead to a reduction of dislocation density, affecting on nucleation rates and growth.

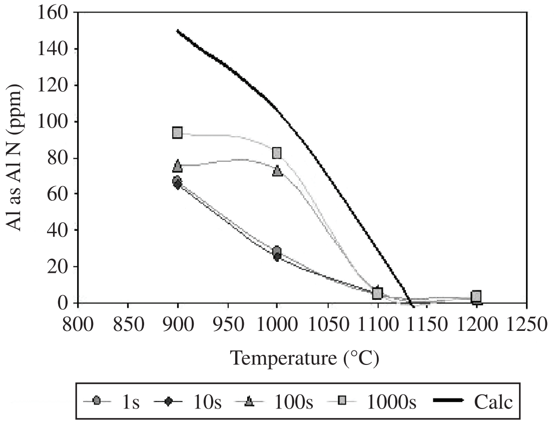


Figure 4. The content of Al as AlN precipitate for the different test temperatures and soaking times.

The differences observed between the present work and the works of Haratani[5] and Oh[6] can be explained based on the chemical composition of silicon steels used in each case, the use of deformation to induce precipitation and the deformation rates applied in the experiments.

Precipitation temperature is determined by solubility product and the relative amounts of ferrite and austenite in the structure. Although the steel used in the present experiment had higher solubility product than in references[5,6], it had higher carbon content and so higher percentage of austenite. The equilibrium temperatures for start precipitation, calculated based on Equations 1 and 2 and the equilibrium fractions of ferrite and austenite, as explained above, were 1288 °C and 18.65%, obtained by Haratani and 1160 °C and 27.50%, obtained by Oh.

The time for precipitation start was studied by Dutta and Sellars[7] and depend on supersaturation, activation energy, deformation and deformation rate. The use of high deformation rate in the present experiment explains the short incubation time compared with the works of Haratani and Oh. In Haratani's experiments no deformation was applied. In Oh's work two deformation rates were used, $3.4 \times 10^{-5}\ s^{-1}$ e $1.1 \times 10^{-1}\ s^{-1}$, which are lower than the deformation rate used in the present work ($0.13\ s^{-1}$). Based on the work of Dutta and Sellars[7], the precipitation start time is proportional to the inverse square root of the deformation rate:

$$t_{ps} \propto \dot{\varepsilon}^{-0.5} \tag{9}$$

In ferrite the recovery rate is higher than in austenite, due to the higher stacking fault energy, and so the start precipitation time can be expressed by[6]:

$$t_{ps} \propto \dot{\varepsilon}^{-0.3} \tag{10}$$

In Figure 6 the precipitation start time obtained in this work is compared with data from Oh's work, with good agreement with the expression above.

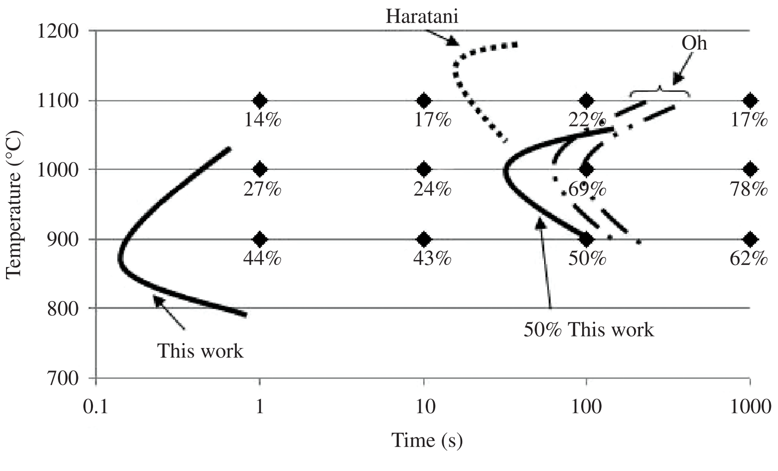


Figure 5. PPT curves for AlN in 3%Si-Fe obtained from this work.

The nitride particles observed in the present work were always associated with sulphide particles, particularly Cu_xS, that tended to precipitate over the AlN particle. A more detailed description of sulphide precipitation kinetics will be the subject of another paper.

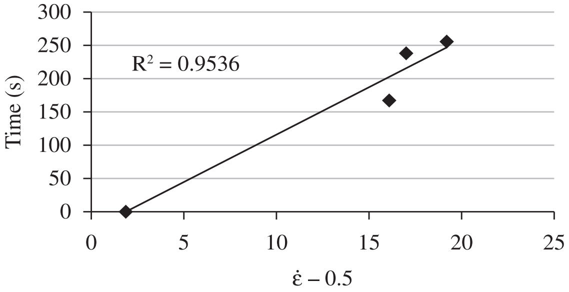


Figure 6. Effect of deformation rate on precipitation start time.

4. Summary

- The PTT diagrams determined by the present compression test for AIN precipitation in the dual-phase 3% Si electrical steel are generally C-shaped, with the nose located under at 900 °C, for time lower than 1 second, and its precipitation doesn't finish before 1000 seconds of test;
- The precipitation start curve obtained here is moved to shorter times because of the chemical composition of silicon steels used and the use of deformation to induce precipitation and the deformation rate applied in the experiments;
- CuS precipitate has a hexagonal close-packed structure and AlN has a face centered cubic structure.

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