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Ion-nitriding behaviour of Fe–Ti alloys in the α-phase region

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The ion-nitriding behaviour of four iron alloys containing between 0.11 and 1.48 wt% titanium was investigated in the α-phase region to discuss kinetics of the growth of the nitriding layer. The ion-nitriding experiments have been made at 823 K. Two nitriding layers were observed: a thin surface layer which mainly consists of Fe_4N; an internal nitriding layer beneath the surface layer, where the nitride formed was found to be TiN. The growth of the internal nitriding layer is controlled by a diffusion process of nitrogen in the matrix metal. The apparent diffusion coefficient of nitrogen in the nitriding layer, evaluated using the rate equation proposed for internal oxidation, increases linearly with the volume fraction of titanium nitride. Furthermore, by excluding the effect of the titanium nitride from the apparent diffusion coefficient, the diffusion coefficient of nitrogen in α-iron was calculated, being in good agreement with that reported so far. In addition, the increase in hardness in the internal nitriding layer has been discussed.

1. Introduction

The ion-nitriding of metals, especially that of iron and steel, is an important surface hardening treatment which is carried out on a large scale in many industries. There are also other nitriding methods for surface hardening, such as gas-nitriding or salt-bath nitriding. However, these methods involve some problems; that is, the former takes a long time to achieve, and the latter generates cyanogen as a by-product.

The ion-nitriding is conducted by setting materials in gas-plasma. The material to be nitrided is put on the cathode, and then the surrounding gas, which consists of H_2 and N_2, is excited using a high voltage, leading to a glow-discharge. Under such conditions, many types of N_iH_j ($i = 1, j = 1 - 5$; $i = 2, j = 2$) ions attack the material and some of them dissolve into the surface region provoking chemical reactions [1].

In the case of the ion-nitriding of iron, a compound layer of iron nitrides is formed on the surface of the material, resulting in an improvement in the mechanical properties of the material [2]. However, in iron alloys with a small amount of alloying element, which forms stable nitrides (for example, titanium or chromium), two kinds of nitriding layers are observed: one on the specimen surface similar to that observed on iron, and the other where the nitride of the alloying element is precipitated in the matrix beneath the compound one [2, 3]. This layer is called the internal nitriding layer, and it also improves the mechanical properties of the material. As yet, the mechanism of ion-nitriding has not been made clear. The purpose of the present work is to study the kinetics of ion-nitriding of Fe–Ti alloys. For this purpose, the effect of the alloying element content on the kinetics of internal nitriding as well as on the hardness increase in the internal nitriding layer were investigated. The nitride formed in the nitrided alloys was also examined by X-ray diffraction.

2. Materials and experimental procedure

Fe–0.11, –0.43, –0.90, and –1.48 wt % Ti alloys were prepared by vacuum melting and hot forging. Their chemical compositions are listed in Table I. Specimens of 5 mm × 5 mm × 10 mm were cut and annealed in a vacuum, yielding a grain diameter of about 100 μm. After being mechanically polished, the specimens were cleaned in an ultrasonic cleaner.

The ion-nitriding of the specimens was made using a tubular furnace equipped with a vacuum pump, electrodes for glow-discharge, and an additional heater for temperature control. The specimens were attached to the electrode as shown in Fig. 1. The temperature of the specimen was measured by a Pt/Pt–13 wt % Rh thermocouple and a potentiometer, and was automatically controlled within ± 4 K.

The ion-nitriding experiments were carried out under the following conditions: glow-voltage, 300 V; glow-current density, 1.9 A m^{-2}; total gas pressure, 1.9×10^3 Pa (14 torr); gas ratio of N_2 to H_2, 0.25; nitriding temperature, 823 K.

Each specimen was rapidly cooled in iced water after the nitriding treatment, and was subsequently cut in half exactly normal to one of the faces of the specimen. The cross-section of each specimen was polished using a buff with alumina powder and then

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TABLE I Chemical compositions of the alloys used (wt %)

Alloy	Ti	C	Si	Mn	P	S
Fe–0.11Ti	0.11	0.0012	0.005	0.003	0.004	0.007
Fe–0.43Ti	0.43	0.0012	0.006	0.003	0.004	0.004
Fe–0.90Ti	0.90	0.0010	0.007	0.005	0.003	0.010
Fe–1.48Ti	1.48	0.0012	0.007	0.007	0.005	0.007

etched by 5% nital. The thickness of the nitrided layer was measured using an optical microscope with a micrometre stage. The hardness was measured using a microvickers hardness tester.

The surface of the nitrided specimen was examined by X-ray diffraction in order to determine the surface layer. Moreover, the nitriding layer was mechanically shaved, and the matrix iron was then chemically removed in a mixture of hydrochloric acid and acetic acid. The residue was examined by X-ray diffraction for the identification of the nitride formed in the nitriding layer.

3. Experimental results

3.1. Microstructure of nitrided specimens

The typical microstructure of Fe–1.48 wt % Ti alloy ion-nitrided at 823 K for 10.8 ksec is shown in Fig. 2, where S indicates the specimen surface and F indicates the internal nitriding front. The nitriding front advances parallel to the specimen surface. The grain boundary seems to have no effect on the growth of the nitriding layer. *E* represents the thickness of the nitriding layer; that is, the distance between S and F. *E* increases as nitriding time increases and as the titanium content decreases. A thin nitride film was observed on the specimen surface of all the specimens used in the present work. The thickness of such a surface layer, *Es*, is so small (only a few micrometres) in comparison with *E* as to be indistinct in Fig. 2. Thus, *Es* was ignored in the analysis of the nitriding kinetics described below.

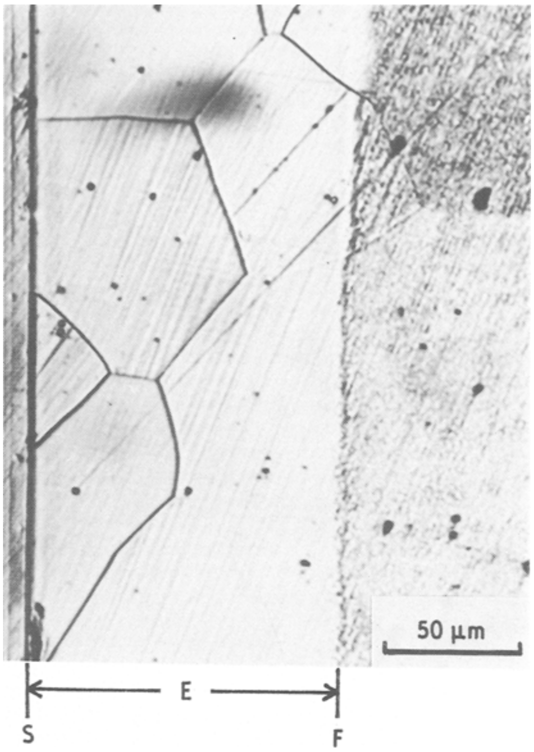

Figure 2 A typical microstructure of Fe–1.48 wt % Ti alloy ion-nitrided at 823 K for 10.8 ksec.

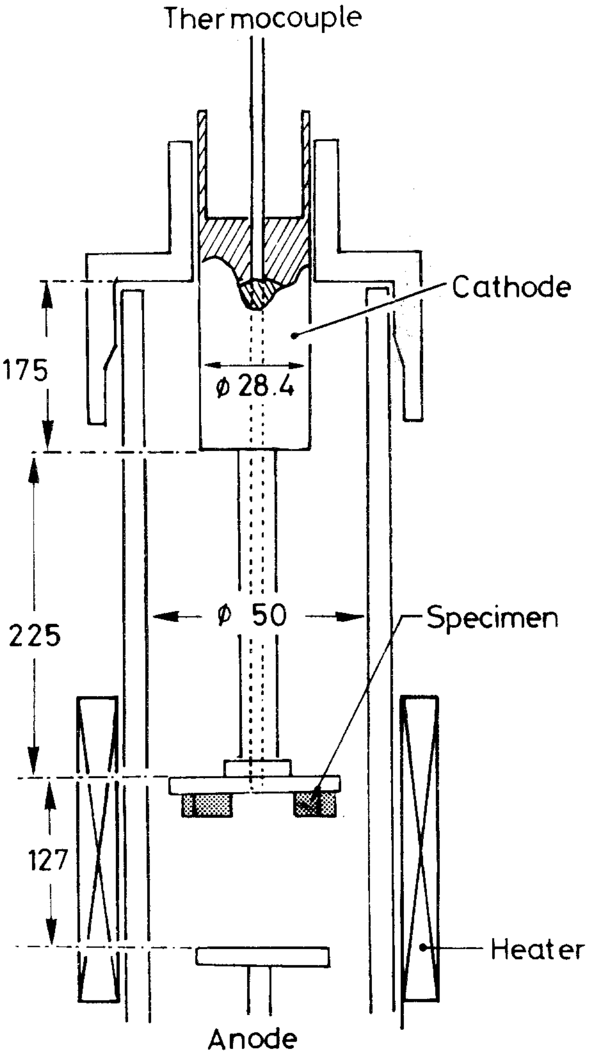

Figure 1 Illustration of ion-nitriding equipment used: specimens are attached to cathode by screws.

From X-ray experiments, the surface film of the present alloys is found to consist of γ'-Fe_4N (f c c) and ε-$Fe_{2-3}N$ (h c p). Edamura [2] has reported that the formation of films in the ion-nitriding of iron alloys depends on the ratio of N_2 to H_2, r, in the gas mixture: in a gas where r equals 0.25, only γ'-Fe_4N film forms; the formation of ε-$Fe_{2-3}N$ as well as γ'-Fe_4N occurs in those gases where r is greater than 0.25. These results agree with those in the present investigation.

Atasoy and Kirkwood [4] have reported that the surface film in Fe–Ti alloys nitrided in an ammonia–hydrogen gas mixture in the temperature range from 787 to 933 K is γ'-Fe_4N, while at temperatures above 933 K the film is ε-$Fe_{2-3}N$. A similar result has been obtained in Fe–V alloys by Bor and Atasoy [5]. Such a transition of the nitride corresponds to the equilibrium diagram of the Fe–N system [6]; γ'-Fe_4N and α-iron is stable below 953 K, while at temperatures above 953 K, ε-$Fe_{2-3}N$ and α-iron are in equilibrium. Thus, the surface layers of neither γ'-Fe_4N nor ε-$Fe_{2-3}N$ are formed to any degree in the gas-nitriding of iron alloys, in contrast to the results of the present study,

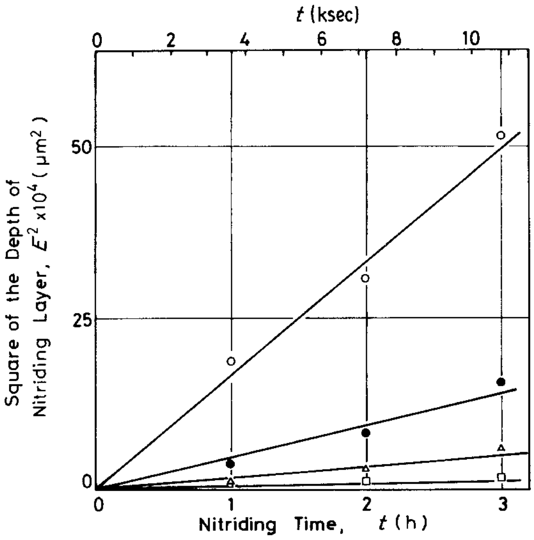

Figure 3 Square of the thickness of the nitriding layer as a function of nitriding time for Fe–Ti alloys nitrided at 823 K. (○) Fe–0.11Ti, (●) Fe–0.43Ti, (△) Fe–0.90Ti, (□) Fe–1.48Ti.

as cited above. These facts suggest that in ion-nitriding, the nitrogen chemical potential of the plasma may be much higher than that predicted from the thermodynamics. That is, the thermodynamic theory may not be appropriate at the plasma–metal interface.

3.2. Rate constant for the penetration of the nitriding front

Fig. 3 shows the square of the thickness, E^2, of the nitriding layer as a function of nitriding time, t, for Fe–Ti alloys nitrided at 823 K. E^2 is proportional to t for each Fe–Ti alloy. Thus, we have a parabolic rate law

$$E^2 = K_p t \qquad (1)$$

where K_p is the rate constant for penetration of the nitriding front. At a constant temperature, K_p decreases as the titanium content increases. These results indicate that the ion-nitriding of the present alloys is controlled by a diffusion process of nitrogen in the matrix metal. This is analogous to the internal oxidation of iron alloys [7–9].

3.3. Identification of the nitride formed in the nitriding layer

Cuddy and Podgurski [10] have found that the nitride in Fe–Ti alloys was TiN, in which the nitride particles were coarsened by annealing above 1073 K after nitriding. On the other hand, nitrides of the alloying element, formed by nitriding below about 1023 K without the subsequent annealing for nitride coasening, have not yet been determined. This is because the particles of titanium nitride are too small in size as well as in amount to be detected by X-ray or electron diffraction [11].

Thus in the present work, the nitride extracted from the internal nitriding layer was examined by X-ray diffraction. The result is shown in Fig. 4. It turned out to be titanium nitride, TiN, the structure of which is f c c.

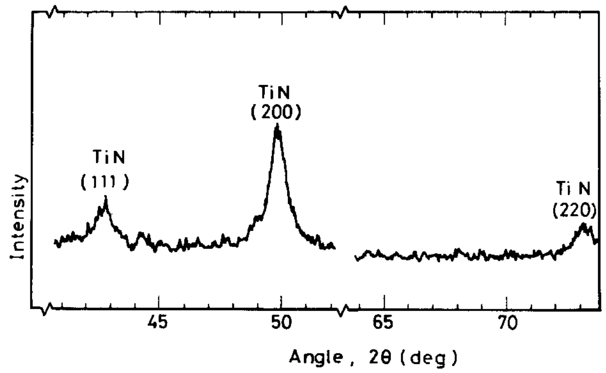

Figure 4 X-ray diffraction for extracted nitride; this shows the presence of titanium nitride, TiN.

3.4. Hardness profile and hardness increment in ion-nitrided Fe–Ti alloys

Fig. 5 indicates the hardness profiles in the ion-nitrided alloys. Fig. 5a shows the effect of nitriding time on the hardness profiles in Fe–0.43 wt % alloy alloy nitrided at 823 K. The hardness of the alloy remains almost constant throughout the nitriding layer and drastically drops at the nitriding front, the position of which is consistent with that determined from the optical observation. The nitriding time has no influence on the hardness of the nitriding layer in each alloy. Fig. 5b shows the hardness profiles of the alloys nitrided at 823 K for 10.8 ksec. One can easily see that, as the titanium content increases, the hardness of the nitriding layer rises markedly in comparison with that of the unnitrided region, the bulk alloy.

ΔHv represents the increase in hardness; that is, the difference in hardness between the internal nitriding layer and the bulk alloy, caused by the dispersed nitride particles; f represents the volume fraction of TiN, which is calculated on the assumption that the alloying element is completely combined with nitrogen in each alloy. Fig. 6 shows ΔHv as a function of the square root of f, giving a linear relationship as follows

$$\Delta \mathrm{Hv} = c f^{1/2} \qquad (2)$$

where c is a constant, the measured value of which is $4.49 \times 10^3\,\mathrm{kg\,mm^{-2}}$.

4. Discussion

4.1. Internal nitriding

As shown in Fig. 3, a parabolic rate law holds for the internal nitriding of Fe–Ti alloys. This suggests that nitrogen in gas-plasma hardly affects the nitriding behaviour of the present alloys, the diffusion of dissolved nitrogen in the metal being the rate controlling process. The kinetics of such nitriding is similar to that of internal oxidation, which has been theoretically discussed by many investigators [12, 13]. Thus, we have applied these theories of internal oxidation in analysing the results of ion-nitriding of the present alloys. We assume that the nitriding reaction takes place completely and instantaneously only at the nitriding front and that the solubility product of the nitride is very low, giving rise to a negligible concentration of dissolved titanium at the nitriding front.

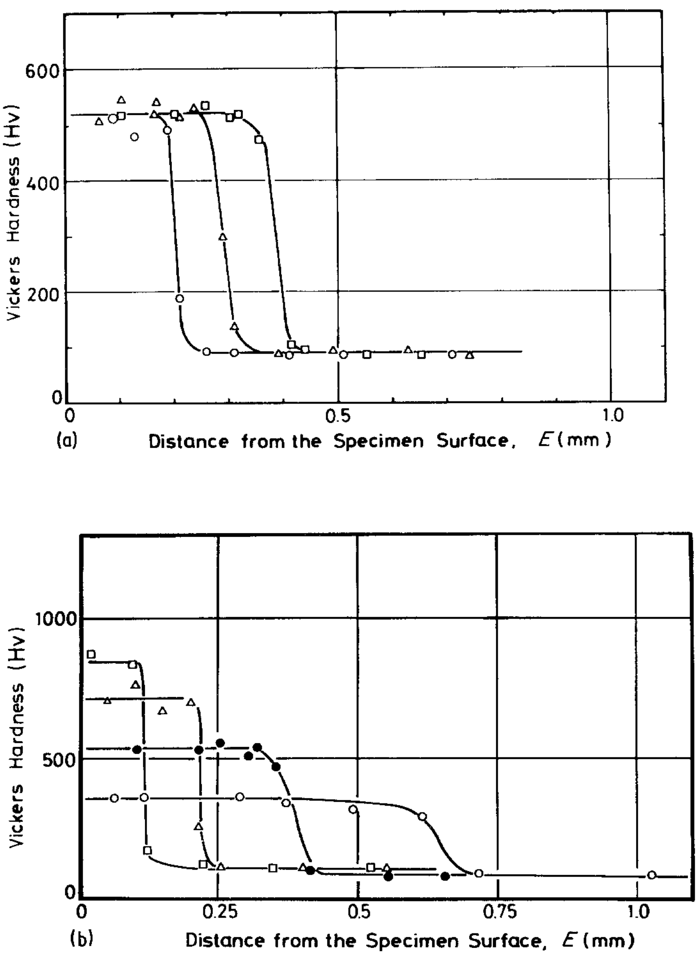

Figure 5 Hardness profiles in the ion-nitrided Fe–Ti alloys: (a) effect of nitriding time for Fe–0.43Ti: (○) 3.6 ksec, (△) 7.2 ksec, (□) 10.8 ksec. (b) Effect of the amount of alloying element for nitriding time of 10.8 ksec: (○) Fe–0.11Ti, (●) Fe–0.43Ti, (△) Fe–0.90Ti, (□) Fe–1.48Ti.

Since the diffusion of titanium is much slower than that of nitrogen, the following equation holds for the penetration of the nitriding front according to that in the internal oxidation [12, 13]

$$E^2 = (2N_N^S D_N^{app}/vN_{Ti})t \qquad (3)$$

where N_N^S is the concentration of nitrogen on the specimen surface, v the atom ratio of nitrogen to titanium, and N_{Ti} the original titanium concentration in the alloy. D_N^{app} is the apparent diffusion coefficient of nitrogen in the internal nitriding layer, where the nitride particles disperse. Because the nitride formed in the nitriding layer is found to be TiN, as shown in Section 3.3, the value of v is 1.0 in the present alloys. If N_N^S is determined either theoretically or experimentally, one can calculate D_N^{app} using Equation 3.

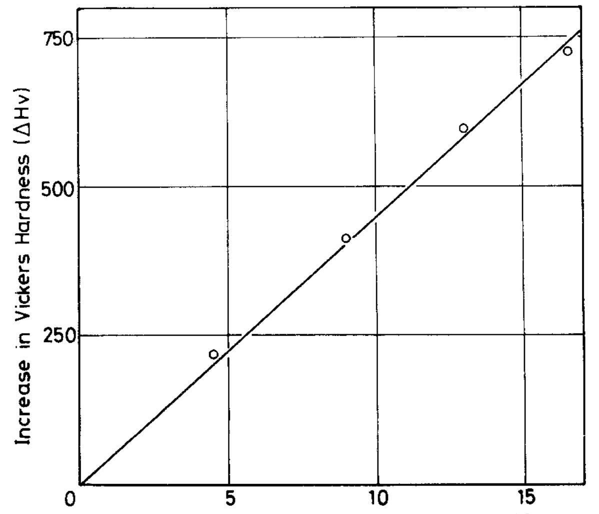

Figure 6 Increase in hardness as a function of the square root of the volume fraction of titanium nitride.

4.2. Nitrogen concentration at the specimen surface

Nitrogen concentration at the specimen surface, N_N^S, has not yet been directly measured in the ion-nitrided alloys. In the present work, ε-$Fe_{2-3}N$ and γ'-Fe_4N were detected on the specimen surface, as described in Section 3.1. In the case of oxidation of iron, several kinds of iron oxide layers (namely, FeO, Fe_3O_4, and Fe_2O_3) are formed on the surface [14]. The atom ratio of oxygen to iron in the inner oxide layer was smaller than that in the outer one; therefore, the matrix iron is thought to be in equilibrium with FeO. If this is taken into consideration when discussing the nitriding behaviour, the matrix iron in the internal nitriding layer would be in equilibrium with the compound layer of γ'-Fe_4N. Thus we take the solubility of nitrogen in α-iron as N_N^S in the present alloys. The solubility is 0.0886 wt % (0.352 at %) at 823 K [15].

4.3. The apparent diffusion coefficient of nitrogen in the internal nitriding layer

D_N^{app}, calculated from the obtained values of K_p, v, N_{Ti}, and N_N^S according to Equation 3, should be distinguished from the diffusion coefficient of nitrogen in α-iron, D_N, since the dispersed nitride particles may affect the nitrogen diffusion.

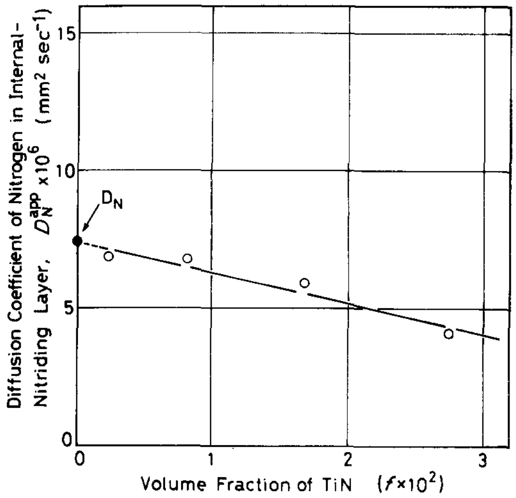

Figure 7 Apparent diffusion coefficient of nitrogen in the internal nitriding layer as a function of the volume fraction of titanium nitride. Nitriding temperature 823 K.

Fig. 7 shows D_N^{app} as a function of the volume fraction of titanium nitride, f. As can be seen in this figure, D_N^{app} decreases as the titanium content increases, and can be expressed as

$$D_N^{app} = D_N + bf \tag{4}$$

where b is a constant. The values of b and D_N determined from the experimental data by the least squares method are -1.11×10^{-4} mm^2 sec^{-1} and 7.47×10^{-6} mm^2 sec^{-1}, respectively. The latter agrees well with the value of diffusion coefficient of nitrogen in α-iron reported by Grieveson and Turkdogan [16]. This fact suggests that the method used in this study is valid in determining D_N. Similar linearity has been obtained for the diffusion coefficient of oxygen in the internal oxidation layer in some iron alloys [8, 9]. However, quite the opposite trend has been observed in these alloys, that is, the diffusion of oxygen is enhanced by the alloying element [8, 9]. Further detailed investigations are necessary to discuss such a different f-dependency of the diffusion coefficient.

5. Conclusions

Ion-nitriding measurements of Fe–0.11, –0.43, –0.90, and –1.48 wt % Ti alloys were made at 873 K in order to study the kinetics of the nitriding layer as well as the hardening behaviour. The results are summarized as follows:

(a) A thin surface layer, mainly consisting of γ'-Fe_4N, was observed with an internal nitriding layer beneath it.

(b) The internal nitriding front advances parallel to the specimen surface. A parabolic rate law holds for the internal nitriding of the present alloys, suggesting that the internal nitriding is controlled by a diffusion process of nitrogen in the matrix metal.

(c) The nitride dispersed in the internal nitriding layer is TiN.

(d) The apparent diffusion coefficient of nitrogen in the nitriding layer, D_N^{app}, calculated using the rate equation for internal oxidation, decreases with the volume fraction of the titanium nitride, f. By extrapolating D_N^{app} to $f = 0$, the diffusion coefficient of nitrogen in α-iron was determined, giving a good agreement with values previously reported.

(e) The difference in hardness between the nitriding layer and the matrix metal increases in proportion to the square root of f.

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