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Effect of peening on structure and volume in a liquid-quenched $Pd_{0.835}Si_{0.165}$ glass

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The radial distribution function (RDF) for x-ray diffraction has been studied for liquid-quenched $Pd_{0.835}Si_{0.165}$ alloy glasses in relation to peening time. The molar volume (V) is obtained from the first peak of the RDF. The longer the peening time, the larger the V (cm^3/mol) becomes. Based on the rate process, we show a linear relationship between V and the peening time (t, expressed in s): $[(V_s-V)/(V_s-V_0)]=1-\exp(-kt)^n$. Here n and k are constants. V_s and V_0 are the volumes of liquid-quenched $Pd_{0.835}Si_{0.165}$ alloy glasses, which are peened for an extremely long period and for 0 s, respectively. V_s agrees with the extrapolated volume of the $Pd_{0.835}Si_{0.165}$ alloy liquid above the melting point.

I. INTRODUCTION

The mechanical, electric, and magnetic properties of liquid-quenched glassy alloys have been investigated.[1-8] However, it is difficult to control these properties homogeneously, because they are radically affected by cooling conditions.

Both peening and aging are homogenizing processes (see Table I). Aging, close to equilibrium, is a good way of homogenizing mechanical and magnetic properties of metallic glasses.[9,10] Although the homogenization relaxes heterogeneous elastic stress induced by liquid quenching, aging usually reduces ductility (Ref. 11) and decreases the magnetic flux density B_s for soft magnetic metallic glasses (Ref. 12).

On the other hand, peening is effective for homogeneously increasing the compressive stress. For commercially used crystal alloys, this stress enlarges the resistance to fatigue (Ref. 13) and stress corrosion (Ref. 14). Furthermore, the dependence of the saturated magnetic flux density B_s and the resistance to plastic deformation (hardness, H_v) of metallic glasses on peening time has been investigated.[15,16] It was seen that the peened and unrelaxed metallic glasses exhibited high B_s and low H_v. Namely, the peening not only enhances the homogeneous stress on the surface of crystal alloys, but also enhances the magnetic properties of metallic glasses. However, the effect has never been investigated systematically. No one has ever studied the peening time dependence of the atomic structure of metallic glasses quantitatively. We have recently examined the cooling-condition dependence of the structure and volume (Ref. 17). With this experience, we have undertaken the present study to observe the effect of peening on the structure, mean atomic distance, coordination number, and molar volume in liquid-quenched $Pd_{0.835}Si_{0.165}$ alloy glasses. The structure is monitored by radial distribution function (RDF) introduced by x-ray diffraction.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

The foil samples of $Pd_{0.835}Si_{0.165}$ were prepared by liquid quenching with a twin-type piston-anvil apparatus under a protective Ar–5 vol % H_2 atmosphere.[18,19] The samples were quenched from approximately 1700 K. The speed of the piston was about 0.12 m/s. The cooling rate, indicated by a parameter D, was changed by controlling the thickness of the samples. Unrelaxed and relaxed glass samples were prepared by fast and slow liquid quenching below the critical thickness to which glass can be prepared. The structure was monitored by x-ray diffraction (model no. RU-200B, Rigaku Denki, Tokyo). The diffraction was performed under a step scanning method (Cu target, 30 kV, 50 mA, 0.05 deg/step, 10 s/step).

B. Peening process

The peening was performed by an apparatus described previously.[15] The nozzle diameter was 8.0 mm. The velocity of air at the nozzle was 195.5 m/s. The distance between the nozzle and the specimen was 20 mm. The peening angle was 30° relative to the specimen. The steel balls were made of SuJ 2 steel [Japan Industrial Standard; $0.95 < C(\text{wt. }\%) < 1.10$, $0.15 < Si(\text{wt. }\%) < 0.35$, $1.30 < Cr(\text{wt. }\%) < 1.60$, hardness of Rockwell C scale H_{RC} is 64]; their mean diameter and weight were 0.4±0.1 mm and 0.68 mg, respectively, and they were supplied at a rate of 18.1 $mg/mm^2\,s$.

C. Analysis of diffraction intensity

The total structure factor $S(Q)$ and radial distribution function $4\pi r^2\rho_0 g(r)$ were obtained from the measured intensity by the following procedures.[20]

The correction of the background was carried out by subtracting the arithmetic mean intensity of the background (I_b) of pure Pd and pure Si from the experimentally measured intensity (I_{expt}). The corrected intensity (I_{corr}) was obtained by dividing $I_{expt}-I_b$ by the product of the absorption (A) and polarization (P) corrections,

$$I_{corr}=I_{expt}/PA\ . \tag{1}$$

P and A are defined as follows:

$$P=(1+\cos^2 2\theta)/2\ , \tag{2}$$

$$A=[1-\exp(-2\mu t\csc\theta)]/2\mu\ , \tag{3}$$

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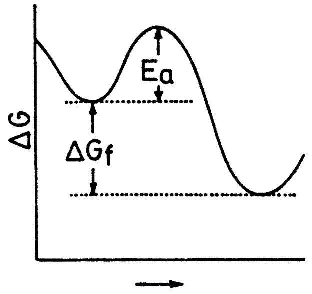
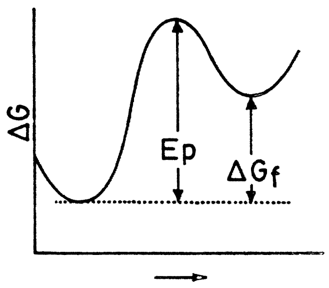
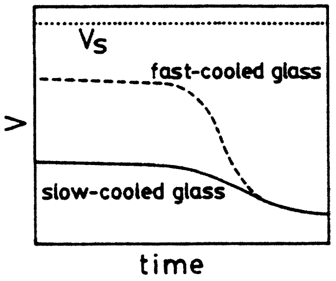
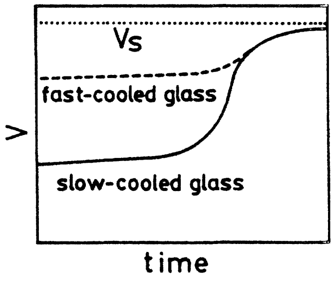
TABLE I. Schematic concepts of rate process of peening and aging.

	Aging	Peening
Structure change	Homogenization	
	(1) stabilization (2) ordering (3) relaxation	(1) destabilization (2) disordering (3) random distribution
Rate processes		
Equation:	$X=1-\exp(kt)^n$	
Energy:	Thermal energy	Collision energy
$X=0$:	glass as quenched	glass as quenched
$X=1$:	relaxed glass ($R\rightarrow 0$)	disordered glass ($R\rightarrow\infty$)
Volume change		

where θ, t, and μ are the scattering angle, the sample thickness, and the linear total absorption coefficient (Ref. 21), respectively. $S(Q)$ was defined by using I_{corr} as follows:

$$S(Q)=(\bar{\beta}I_{\text{corr}}-\langle f^2\rangle+\langle f\rangle^2-I_{\text{inc}})/\langle f\rangle^2\ , \tag{4}$$

$$Q=4\pi(\sin\theta)/\lambda\ , \tag{5}$$

where $\bar{\beta}$, f, and λ are the conversion factor, the total atomic scattering factor, and the x-ray wavelength of 0.154 18 nm (Ref. 22), respectively. I_{inc} is the Compton scattering intensity, which uses the results by Compton and Allison.[23] f was given by the following equation:[24,25]

$$f=\sum_{i=1}^{4}a_i\exp(-b_i\sin^2\theta/\lambda^2)+C+f'+f''\ , \tag{6}$$

where a_i, b_i, and C are the coefficients for the atomic scattering factor. f' and f'' are the real and imaginary components of the anomalous dispersion. In the generalized Krogh-Moe-Norman method, the conversion factor (Ref. 26) was given by

$$\bar{\beta}=\left[\int_0^{Q_{\max}}Q^2[(\langle f^2\rangle+I_{\text{inc}})/\langle f\rangle^2]\exp(-RQ^2)dQ-2\pi^2\rho_0\right]\Big/\left[\int_0^{Q_{\max}}Q^2(I_{\text{corr}}/\langle f\rangle^2)\exp(-RQ^2)dQ\right]\ , \tag{7}$$

$$Q=4\pi(\sin\theta)/\lambda\ , \tag{8}$$

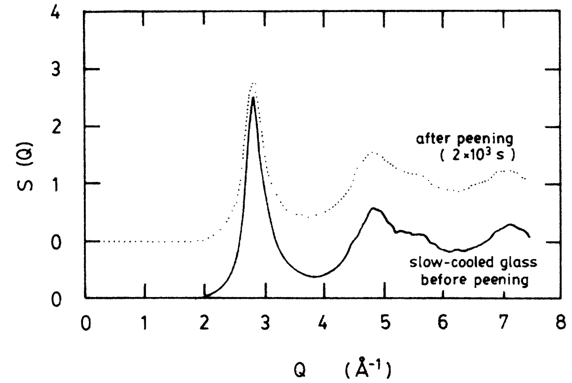


FIG. 1. $S(Q)$ change with Q of slow-cooled $Pd_{0.835}Si_{0.165}$ alloy glasses peened for 0 and 2000 s.

where Q_{max} is the Q at the scattering angle ($2\theta = 133°$), R is the damping factor [$R = 0.01$ (Ref. 27)], and ρ_0 is the atomic number density of the sample.

The radial distribution function (D_{RDF}) was obtained as a Fourier transform of $S(Q)$,

$$D_{RDF} = 4\pi r^2 \rho_0 g(r) = 4\pi r^2 \rho_0 + (2r/\pi) \int_0^{Q_{max}} Q[S(Q)-1]\sin(Qr)dQ \ . \tag{9}$$

The coordination number was calculated from the area under the first peak in the RDF as follows:

$$n = \int_{r'}^{r''} 4\pi r^2 \rho_0 g(r) dr \ , \tag{10}$$

where r' was the value below which the RDF is zero, and r'' was the position of the first minimum of the RDF. In other words, although the first peaks of Pd-Pd and Pd-Si of this wavelength cannot be divided, the mean coordination number (n) was obtained by the area of first peak of RDF.

III. RESULTS

A. $S(Q)$, RDF, and atomic distance

Figure 1 shows $S(Q)$'s of Pd-Si glassy alloys obtained for different peening times. The high, narrow first peak and the split second peak are noteworthy in the $S(Q)$ of the slow-quenched glass before peening in comparison with that of the peened glass. The longer the peening time, the lower and broader the first peak becomes, as shown in Figs. 2(a) and 2(b).

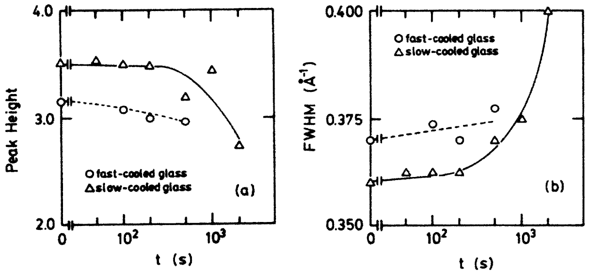


FIG. 2. Changes in (a) peak height and (b) half-value width (full width at half maximum) of $S(Q)$ with peening time (t) of $Pd_{0.835}Si_{0.165}$ alloy glasses.

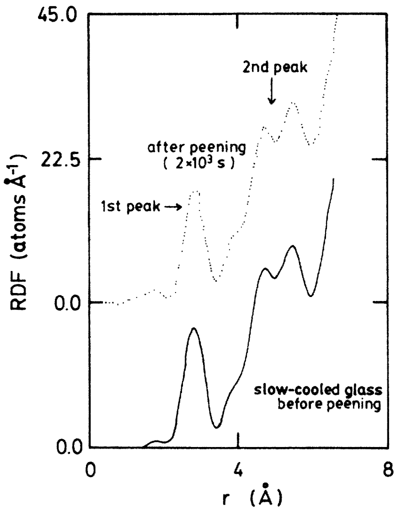


FIG. 3. Radial distribution function changes with atomic distance of slow-cooled $Pd_{0.835}Si_{0.165}$ alloy glasses peened for 0 and 2000 s.

Figure 3 shows RDF's as Fourier transforms of $S(Q)$'s. The remarkably split second peak and the high, narrow first peak are found in the RDF of the slow-quenched glass before peening. The dotted line indicates the peened glass after 2000 s. The longer the peening time, the lower and broader the first peak becomes.

Figure 4 shows the changes in the mean atomic distance (r_1) with the peening time (t). The slow-quenched glass shows small r_1. r_1 increases with the increase in peening time. The present results are of the same order of magnitude as the results previously obtained for r_1 change according to cooling conditions [$2.828 < r_1 < 2.835$ Å (Ref. 17)].

B. Coordination number

Figure 5 shows the change in the total coordination number n with the peening time t. n decreases as t in-

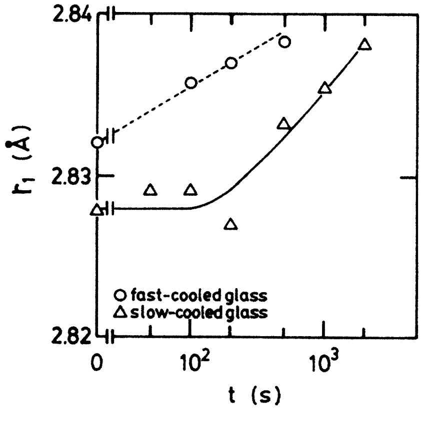


FIG. 4. Changes in mean atomic distance (r_1) of first peak in RDF with peening time (t) of $Pd_{0.835}Si_{0.165}$ alloy glasses.

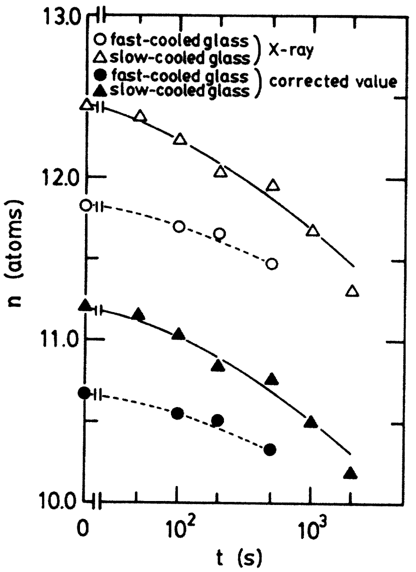


FIG. 5. Changes in total coordination number (○,△) and corrected coordination number (●,▲) with peening time (t) of fast- and slow-cooled $Pd_{0.835}Si_{0.165}$ alloy glasses. ○ and ● are for fast cooled glasses. △ and ▲ are for slow-cooled glasses.

creases. Neutron diffraction analysis revealed the existance of separated first peaks (see Fig. 6). Both peaks are for Pd-Pd atoms and Si-Si atoms. The coordination numbers of Pd-Pd atoms ($n_{\text{Pd-Pd}}$) and Si-Si atoms ($n_{\text{Pd-Si}}$) are 10.6 ($15.5 < \text{at.\%}$ Si<20) and 1.38 [$n_{\text{Pd-Si}} = 7.58 \times 10^{-2}$ (at.% Si)$+0.133$; $15.5 < \text{at.\%}$ Si<20] for the

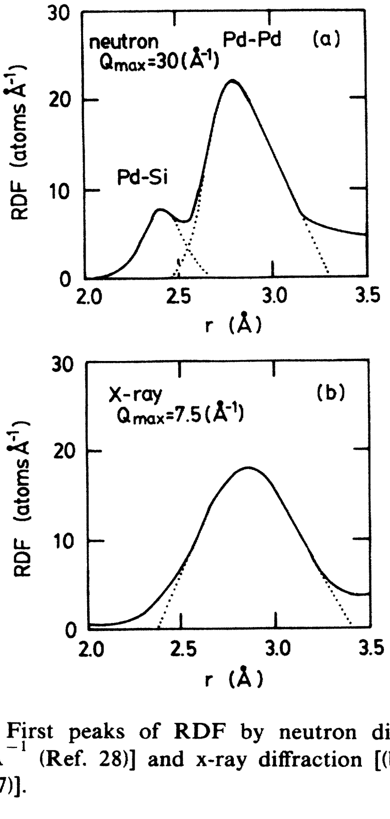


FIG. 6. First peaks of RDF by neutron diffraction [(a) $Q_{\max} = 30$ Å^{-1} (Ref. 28)] and x-ray diffraction [(b) $Q_{\max} = 7.5$ Å^{-1} (Ref. 17)].

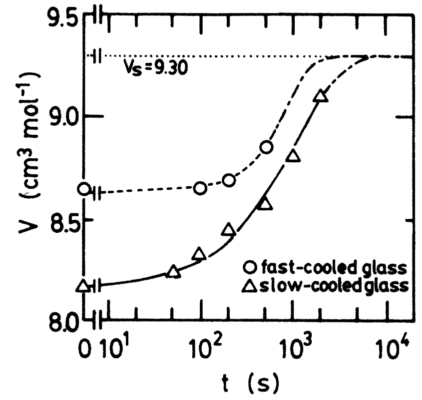


FIG. 7. Changes in molar volume (V) with peening time (t) of $Pd_{0.835}Si_{0.165}$ alloy glasses. Solid line is for slow-cooled glass. Dotted line is for fast-cooled glass. V_s is molar volume of glass peened to infinity.

fast-quenched glass produced by a roll-quenching method.[28,29]

Based on metallographic analysis (changes in mean distance of dendrite and crystal orientation), the cooling condition of the piston-anvil method can be assumed to be nearly equal to that of the roll-quenched method for the thin and fast-quenched specimens of Al-Cu alloys, though both methods show different conditions at the same sample thickness for slow-cooled specimens.[30] Therefore, n for x rays is assumed to relate to $n_{\text{Pd-Pd}}$ (10.6) for the fast-quenched $Pd_{0.835}Si_{0.165}$ glass ($D = 0.06$ mm). If the fraction ($n/n_{\text{Pd-Pd}} = 1.10$ for Pd–16.5 at.% Si alloy glass) does not depend on the cooling condition and peening time, the change in $n_{\text{Pd-Pd}}$ is as shown in Fig. 5 (see dotted line). $n_{\text{Pd-Pd}}$ increases as D increases. The present results ($11.30 < n < 12.47$, $10.19 < n_{\text{Pd-Pd}} < 11.25$) are of the same order of magnitude as the results of n change with cooling condition (Ref. 17; $11.75 < n < 12.59$, $10.60 < n_{\text{Pd-Pd}} < 11.35$).

IV. DISCUSSION

A. Molar volume (V)

Atomic volume V is estimated by the coordination number (n), the first-nearest distance between atoms (r_1), and the following equation:[26,31–33]

$$V/V' = (r_1/r_1')^3(n'/n) . \tag{11}$$

n and r_1 are measured by the RDF of x-ray diffraction. r_1' and n' are the values when the molar volume (V') is known. V' is calculated from the density of the fast-quenched Pd-Si alloy glass ($Pd_{0.835}Si_{0.165}$ alloy glass, $0.02 < D < 0.06$ mm, roll-quenched method):[34]

$$[V'-V(\text{Pd}-14.5\text{ at. \% Si glass})]/[V(\text{Pd}-14.5\text{ at. \% Si glass})-V(\text{Pd}-19.8\text{ at. \% Si glass})]=0.337 . \quad (12)$$

Taking into account changes in mean distance of dendrite and crystal orientation, the cooling condition of the piston-anvil method can be assumed to be nearly equal to that of the roll-quenched method for the thin and fast-quenched specimens, though the cooling conditions of both methods are different at the same D for the slow-quenched specimens.[30] Therefore, V' is assumed to be 8.74 cm^3/mol for the fast-quenched $\text{Pd}_{0.835}\text{Si}_{0.165}$ glass ($D=0.06$ mm).

Figure 7 shows the change in molar volume (V) with peening time (t). The slow-quenched glass shows small V. That is, the longer the peening time, the larger V becomes.

B. Rate process

If the energy involved in peening is collision energy, a rate process can be applied (see Table I). Based on the rate process,[35] the volume-fraction change (X) is generally expressed by the following equation in relation to the peening time (t expressed in s),

$$X=1-\exp(-kt)^n . \quad (13)$$

Here, k and n are constant. X is assumed to express

$$X=[(V_s-V)/(V_s-V_0)] , \quad (14)$$

where V_s and V_0 are volumes of glass peened for extremely long periods of time and of glass before peening, respectively. Here, V_s of Eq. (14) is 9.30 cm^3/mol, when the correlation coefficient (F) of Eq. (13) is maximum ($F=0.9895$) as shown in Fig. 8.

From these results, X is expressed by the following equation of slow-cooled Pd–16.5 at. % Si alloy glasses (see Fig. 9):

$$\log_{10}[-\ln(1-X)]=0.848\log_{10}t-2.57 . \quad (15)$$

This linear plot confirms the assumption of Eq. (13). V (cm^3/mol) is plotted for slow-cooled $\text{Pd}_{0.835}\text{Si}_{0.165}$ alloy glasses (see solid line in Fig. 6). V of the peened glass approaches V_s in Fig. 6. V_s is larger than the extrapolated volume of the extremely fast-cooled glass [$V_e=8.98$ cm^3/mol (Ref. 17)], whereas V_s is quite close to the extrapolated volume of the $\text{Pd}_{0.835}\text{Si}_{0.165}$ liquid [9.39 cm^3/mol (Ref. 36)]. Although the present results ($8.372<V<9.115$ cm^3/mol) for changes by peening are of the same order of magnitude as the volume changes with the cooling condition (Ref. 17; $8.169<V<8.738$ cm^3/mol), the excess volume is explained by the excess defects introduced by the peening. In other words, both peening and rapid quenching seem to introduce different defects to a similar degree.

If the volume of the liquid is assumed to be V_s, X is expressed by the following equation for the fast-cooled Pd–16.5 at. % Si alloy glasses:

$$\log_{10}[-\ln(1-x)]=0.823\log_{10}t-2.56 . \quad (16)$$

Since F (the correlation coefficient) in this assumption is 0.9892, the extrapolated value is probably used as V_s (see Fig. 7).

The effects of peening on the mean atomic distance (Fig. 4), coordination number (Fig. 5), and molar volume (Fig. 7) were investigated for fast-cooled glass. Although the changes were smaller than those for slow-cooled glass, they were found to be similer.

V. CONCLUSION

The RDF change with peening was studied for liquid-quenched glass. The peened glasses showed the larger atomic distances, small coordination numbers, and larger molar volumes (V expressed in cm^3/mol.).

If the energy involved in peening is collision energy, a rate process can be applied (see Table I). Based on the

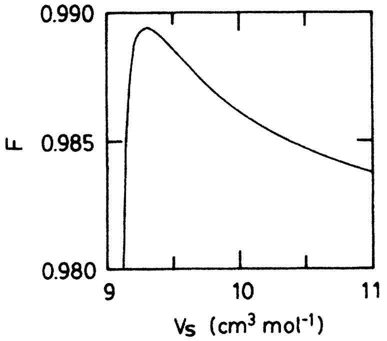


FIG. 8. Changes in correlation coefficient (F) with V_s. V_s is molar volume of slow-cooled glass peened to infinity.

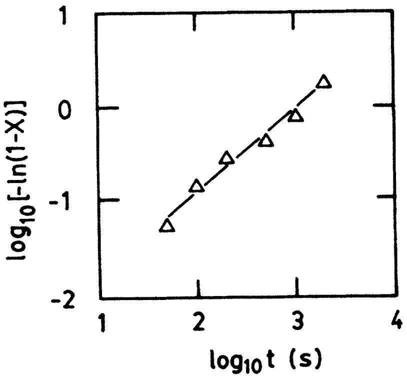


FIG. 9. Linear plot between $\log_{10}[-\ln(1-X)]$ and peening time (t) of slow-cooled $\text{Pd}_{0.835}\text{Si}_{0.165}$ alloy glasses, where V is molar volume.

rate process, the volume-fraction change (X) is generally expressed by the following equation in relation to the peening time (t expressed in s):

$$X = 1 - \exp(-kt)^n .$$

Here, k and n are constant. n and $\log_{10}k$ of Pd−16.5 at. % Si alloy glasses are 0.848 and −2.57, respectively. X is assumed to be $(V_s - V)/(V_s - V_0)$, where V_s and V_0 are volumes of glass peened for extremely long periods of time and of glass before peening, respectively. Here, V_s is 9.30 cm^3/mol, when the correlation coefficient (F) is maximum ($F = 0.9895$). V_s is quite close to the extrapolated volume of $Pd_{0.835}Si_{0.165}$ liquid.

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