Damping Capacity, Magnetic and Mechanical Properties and Corrosion Resistance of Fe-Co-Mo-Cr Alloys*

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The damping capacities, magnetic and mechanical properties and corrosion resistances have been investigated in Fe-Co-Mo-Cr alloys. Measurements of the internal friction, the magnetic hysteresis loop and the tensile strength were carried out using an inverted torsion pendulum, an automatic recording flux-meter and an Instron-type machine, respectively. The anodic polarization characteristics in 3% NaCl and 5% H₂SO₄ solutions were measured by the moving potential method using a potentiostat.

The maximum value of internal friction $Q_{\max}^{-1}$ depends largely on the change in magnetic properties with alloying composition and heat treatment. In the case of Fe-Co-Mo-Cr alloys containing 20% Cr, fairly high values of $Q_{\max}^{-1}$ greater than 50×10^{-3} are obtained upon furnace cooling in the composition range of Co of 2–4.5% and Mo less than 2.5%, and are obtained upon water quenching in the composition range with Co less than 6.5% and Mo less than 9.5%.

The Fe-Co-Mo-Cr alloys with high $Q_{\max}^{-1}$ show the microstructure of α single phase and have a moderately small H_c , whereas those with very low $Q_{\max}^{-1}$ show the microstructure of two phases and have a very large H_c . Therefore, the larger the magnetic hysteresis loss at a small strain amplitude, the higher the $Q_{\max}^{-1}$.

The tensile strength and the yield strength of the alloys with 4% Co and 20% Cr increase with increasing Mo concentration, while the elongation decreases. The corrosion resistances of pitting and sulfuric acid are improved by the addition of Mo, because the pitting potential in NaCl solution increases sharply and the critical current density for passivation in H₂SO₄ solution decreases rapidly.

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I. Introduction

Recently, the applied study on the high damping alloys has been actively reported for the purpose of minimization or prevention of various damages suffered by vibration and noise. Applications of the Fe-base alloys are expected in as many wide fields as the Ni-base alloys because of their high damping capacity, excellent mechanical strength and good workability⁽¹⁾⁻⁽⁴⁾. Moreover, development of

the high damping alloys with the corrosion resistance may be required in many corrosive applications.

The present authors have already reported on the damping capacity, mechanical properties and pitting resistance of the Fe-Mo-Cr and Fe-Co-Cr alloys⁽⁵⁾⁽⁶⁾. It has been made clear from the experimental results that the damping capacity is closely related to the magnetic properties accompanying the microstructures which are changed by alloying composition and by heat treatment. Namely, the damping capacity is higher when the alloys show α single phase (ferrite) and show a moderately small coercive force, whereas it is very low when the alloys show two phases of α and σ or χ and show a fairly large coercive force. Further, the pitting resistance of the alloys with α single phase is favorable, while the pitting for the alloys with two phases occurs easily for lack of Cr in the matrix.

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The present paper describes the variations in damping capacity, magnetic and mechanical properties and corrosion resistances of pitting and sulfuric acid of the Fe-Co-Mo-Cr alloys with heat treatment and alloying composition.

II. Experimental

The chemical compositions of 99.9% (mass%) purity Fe and Mo, 99.7% Cr and 99.6% Co used as raw materials are listed in Table 1. For the preparation of specimens, the metals 0.8 kg in total weight were melted with a deoxidizing element and flux using a high frequency furnace while flowing argon gas. The resulting ingots 25 mm in diameter were hot-forged to the wires 6 mm in diameter and to the plates 10 mm thick and 20 mm wide, respectively. The wires were cold-swaged and drawn to 2.0 mm diameter for the tensile test and to 0.8 mm diameter for the damping capacity and hysteresis loop measurements. On the other hand, the plates were cold-rolled to 3 mm thick for the pitting and sulfuric acid corrosion tests. The wires were straightened, and the plates were polished up to #400 by waterproof emery paper. The specimens thus prepared were heated in a vacuum for 7.2 ks at 1173, 1273 and 1373 K and then furnace-cooled, air-quenched and water-quenched, respectively. The specimens used were in the composition range of 2–8% Co, 1–9% Mo and 10–25% Cr.

The plate specimens were soldered with copper lead wires on the back area, embedded in epoxy resin and then again polished up to #600.

To prevent the crevice corrosion in the pitting corrosion test, the method of Shiobara *et al.*⁽⁷⁾ was used. The abraded surface was passivated in the solutions of 20% to 30% HNO₃ at temperatures from 303 K to 343 K and covered with double insulating films, leav-

ing a testing area of 1 cm². Finally, the testing area was abraded by #600 emery paper.

For the damping capacity measurements, the decay curve of vibration was measured at a frequency of about 1 Hz using the inverted torsion pendulum method⁽⁸⁾⁽⁹⁾. The decay curve was detected using the CdS photo-bridge method⁽¹⁰⁾ or the galvanometer method⁽¹¹⁾, and it was memorized by a Transient Time Converter. The internal friction was calculated by using a computer for the curve. The magnetic hysteresis loop was measured by an automatic recording fluxmeter, and the tensile test was carried out by means of an Instron-type machine.

During the pitting and sulfuric acid corrosion tests, the anodic polarization curves were measured by the moving potential method using a potentiostat⁽¹²⁾. The solutions of 3% NaCl and 5% H₂SO₄ were deoxidized by flowing high purity argon gas prior to the tests and then were kept at a temperature of 298 K during the tests. All potentials were measured with respect to a saturated calomel electrode, and the potential scanning rates were 0.306 mV/s and 1.224 mV/s.

III. Results and Discussion

1. Internal friction

The internal friction of the ferromagnetic alloys is dependent on the amplitude of vibration, and becomes higher with the increase in maximum shear strain-amplitude γ_m . It then passes through a maximum and then decreases. It is due to the magnetomechanical effect of ferromagnetic alloys that the internal friction Q^{-1} shows the maximum value $Q_{\max}^{-1}$ against the γ_m . The magnitude of $Q_{\max}^{-1}$ and γ_m at which the $Q_{\max}^{-1}$ appears may be determined by the magnetic properties (hysteresis loss,

Table 1 Chemical composition of the starting materials (mass%).

Metals	Ni	Fe	Mn	Si	Al	Cu	C	S	P
el. Fe	—	—	0.006	0.005	—	0.004	0.005	0.005	0.004
el. Co	0.140	0.150	0.012	0.025	—	—	0.007	0.004	—
mt. Mo	0.020	0.030	—	0.010	0.005	0.003	—	0.001	0.004
mt. Cr	—	0.110	—	0.070	0.060	—	0.030	0.020	0.010

Fig. 1 Maximum value of internal friction $Q_{\max}^{-1}$ of Fe-Co-Mo-Cr alloys containing 20% Cr furnace-cooled after heating at (a) 1273 K and (b) 1373 K for 7.2 ks.

coercive force and magnetostriction and others) and the mechanical properties⁽³⁾⁽¹³⁾. Furthermore, the internal friction of the Fe-Mo-Cr and Fe-Co-Cr alloys shows a high value over a wide range of composition, and the corrosion resistance of these alloys becomes favorable with the increase in Cr, Mo and Co concentrations⁽⁵⁾⁽⁶⁾.

Figure 1 represents the contour lines of $Q_{\max}^{-1}$ against the composition of the Fe-Co-Mo-Cr alloys containing 20% Cr furnace-cooled after heating at 1273 K (a) and 1373 K (b) for 7.2 ks. In the figure, the composition of the specimens used is indicated by solid circles, and the values reported previously were used for the ternary alloys⁽⁵⁾⁽⁶⁾. In the case of heating at 1273 K, a

range of $Q_{\max}^{-1}$ greater than 30×10^{-3} is obtained in the composition range with 1–4.5% Co and Mo less than 2.5%. When heated at 1373 K the $Q_{\max}^{-1}$ becomes wholly higher because of the growth of grains, and a range of $Q_{\max}^{-1}$ greater than 50×10^{-3} appears in the composition of Co of 2–4.5% and Mo less than 2.5%.

In the figure above, the alloys in the range with high $Q_{\max}^{-1}$ show the microstructure of the α (ferromagnetic) single phase. On the other side, the alloys containing a small amount of Co and a large amount of Mo in the range with low $Q_{\max}^{-1}$ show the microstructure of two phases which an intermetallic compound χ phase precipitates in the matrix of α phase, whereas those containing a large amount of Co and a small amount of Mo in the range with low $Q_{\max}^{-1}$ show the α phase in which the residual strain due to the γ - α transformation is large⁽⁵⁾⁽⁶⁾. Besides, the values of $Q_{\max}^{-1}$ in the range with small amounts of Co and Mo become somewhat lower because of the microstructure which the σ phase precipitates merely in the matrix.

The contour lines of $Q_{\max}^{-1}$ against the composition are shown in Fig. 2 for the same alloys as given in Fig. 1 but were water-quenched after heating at 1273 K (a) and 1373 K (b) for 7.2 ks. In the case of heating at 1273 K, the $Q_{\max}^{-1}$ is generally higher in Fig. 2 than the case of furnace cooling in Fig. 1. The values greater than 50×10^{-3} are obtained in the composition range with Co and Mo less than 4.5% and 6% in Fig. 2. The range of $Q_{\max}^{-1}$ greater than 50×10^{-3} becomes wider upon heating at 1373 K than at 1273 K and appears in the composition with Co less than 6.5% and Mo less than 9.5%. The alloys with Co and Mo greater than these amounts show the relatively low values of $Q_{\max}^{-1}$ upon furnace cooling, and the fairly high values in Fig. 2 because the α phase is brought by water quenching.

Figure 3 shows the effect of Mo concentration on the $Q_{\max}^{-1}$ of the Fe-Co-Mo-Cr alloys containing 2% Co and 20% Cr when furnace-cooled (a), air-quenched (b) and water-quenched (c) after heating at 1173, 1273 and 1373 K for 7.2 ks. In the case of furnace cooling, the $Q_{\max}^{-1}$ values become gradually higher with the increase in Mo more than 2% but are very low

Fig. 2 Maximum value of internal friction $Q_{\max}^{-1}$ of Fe-Co-Mo-Cr alloys containing 20% Cr water-quenched after heating at (a) 1273 K and (b) 1373 K for 7.2 ks.

at Mo concentrations of 5, 6 or 7% when heated at 1173 K, 1273 K or 1373 K, respectively. On the other hand, the $Q_{\max}^{-1}$ values in both cases of air quenching and water quenching are higher than those in the case of furnace cooling. Particularly, when heated at 1373 K, the values become considerably higher with increasing Mo concentration. This may be attributed to the formation of the α solid solution is carried out as a result of the suppression of precipitation of the σ and χ phases by rapid cooling. Here, if the amount of Mo is significant, the α phase consists of the supersaturated solid solution. Furthermore, the $Q_{\max}^{-1}$ values in all states become higher with the rise in the heating temperature because of the growth of

Fig. 3 Maximum value of internal friction $Q_{\max}^{-1}$ as a function of Mo concentration in Fe-Co-Mo-Cr alloys containing 2% Co and 20% Cr: (a) furnace-cooled, (b) air-quenched and (c) water-quenched after heating at 1173 K ($\circ$ — $\circ$), 1273 K ($\triangle$ — $\triangle$) and 1373 K ($\bullet$ — $\bullet$) for 7.2 ks.

crystal grains. In the case of heating at 1373 K, it may be due to the mere increase in the strain caused by quenching that the $Q_{\max}^{-1}$ values upon water quenching are somewhat lower than those upon air quenching.

Figure 4 indicates the effect of Mo concentration on $Q_{\max}^{-1}$ in the Fe-Co-Mo-Cr alloys containing 4% Co and 20% Cr subjected to the same heat treatment as shown in Fig. 3. The value of $Q_{\max}^{-1}$ becomes higher with the rise in heating temperature. Its variation with Mo concentration is also similar to that of the alloys containing 2% Co given in Fig. 3, but in the case of furnace cooling (c) a considerably higher value is shown at 3–6% Mo. The increment in $Q_{\max}^{-1}$ may be connected with the decrease in precipitation of the σ phase and the increase in solubility of Mo when the Co concentration increases. However, the addition of more than ca. 6% Co to this alloy system is not appropriate because Co is an austenitic (non-ferromagnetic) element.

As mentioned above, $Q_{\max}^{-1}$ is closely related

Fig. 4 Maximum value of internal friction $Q_{\max}^{-1}$ as a function of Mo concentration in Fe-Co-Mo-Cr alloys containing 4% Co and 20% Cr: (a) furnace-cooled, (b) air-quenched and (c) water-quenched after heating at 1173 K ($\circ$), 1273 K ($\triangle$) and 1373 K ($\bullet$) for 7.2 ks.

to the microstructures brought about by the heat treatments, being high in the α single phase state and low in the two-phase state. That is, $Q_{\max}^{-1}$ may be determined by the magnetic properties associated with the microstructures as will be mentioned in the following⁽⁶⁾⁽¹³⁾.

2. Magnetic properties

Figure 5 represents the effect of the Mo concentration on the coercive force H_c for the alloys containing 2% Co and 20% Cr when subjected to the same heat treatment as given in Fig. 3. In the case of furnace cooling, the H_c values at 1273 K or 1373 K increase sharply when the increase in Mo is more than 6 or 7%. On the other hand, in the cases of air quenching and water quenching, the H_c at 1273 K increases sharply with more than 7% Mo, but when heating at 1373 K shows a small value even with 8% Mo. The H_c values become generally smaller with the decrease in stress but become larger when the alloys change from the

Fig. 5 Coercive force H_c as a function of Mo concentration in Fe-Co-Mo-Cr alloys containing 2% Co and 20% Cr: (a) furnace-cooled, (b) air-quenched and (c) water-quenched after heating at 1173 K ($\circ$), 1273 K ($\triangle$) and 1373 K ($\bullet$) for 7.2 ks.

single to two phases.

Figure 6 represents the effect of Mo concentration on H_c in the same alloys containing 4% Co and 20% Cr as given in Fig. 4. As seen in the figure, the variation in H_c with heating temperature and Mo concentration is similar to the case of the alloys containing 2% Co (Fig. 5). As compared Figs. 3 and 4 with Figs. 5 and 6, it is obvious that the $Q_{\max}^{-1}$ shows a higher value at a relatively small H_c value of 0.05–0.2 kA/m, whereas it shows a considerably lower value at large H_c of 0.5 kA/m or above.

The magnetic induction, B , of these alloys decreases gradually with increasing Mo concentration, and the B of the alloys with large H_c is not saturated because the displacement of the magnetic domain wall can hardly be caused in the magnetic field H of 23 kA/m.

Now, let us consider the relation between the Q^{-1} and the magnetic properties. When the vibrational stress is applied, the Q^{-1} can be explained in terms of $\Delta W/2W$, where ΔW is the energy dissipated during a complete oscillatory cycle and W is the vibrational (elastic) energy. Here, ΔW corresponds to the magnetic

Fig. 6 Coercive force H_c as a function of Mo concentration in Fe-Co-Mo-Cr alloys containing 4% Co and 20% Cr: (a) furnace-cooled, (b) air-quenched and (c) water-quenched after heating at 1173 K ($\circ$ — $\circ$), 1273 K ($\triangle$ — $\triangle$) and 1373 K ($\bullet$ — $\bullet$) for 7.2 ks.

hysteresis loss W_h which becomes sharply larger with the increase in H and becomes constant with the saturation in B . On the other hand, W is proportional to the $\gamma_m^2 \times G$ and increases with increasing γ_m , where G is the rigidity modulus.

Consequently, the Q^{-1} shows a maximum value $Q_{\max}^{-1}$ against the γ_m . The displacement of domain wall for the alloys with small H_c can easily be caused by small γ_m from the inverse effect of magnetostriction because the H_c is proportional to $\gamma_c \times G^{0.5}$, where the γ_c is the value of γ_m in which the $Q_{\max}^{-1}$ appears⁽³⁾. Therefore, the $Q_{\max}^{-1}$ of the ferromagnetic alloys becomes higher in the state which the B and W_h become larger at small γ_m by the irreversibility of magnetization. However, the $Q_{\max}^{-1}$ of the alloys with large H_c becomes lower because the magnetization is hardly caused at ordinary level of γ_m and the W_h is very small.

3. Mechanical properties

Figure 7 shows the effect of Mo concentra-

Fig. 7 Tensile strength σ_t , yield strength σ_y and elongation E_l as a function of Mo concentration in Fe-Co-Mo-Cr alloys containing 4% Co and 20% Cr: (a) furnace-cooled and (b) water-quenched after heating at 1273 K ($\circ$ — $\circ$) and 1373 K ($\bullet$ — $\bullet$) for 7.2 ks.

tion on the tensile strength σ_t , the yield strength σ_y and the elongation E_l for the same alloys as shown in Fig. 4 when furnace-cooled (a) and water-quenched (b) after heating at 1273 K and 1373 K for 7.2 ks. The values of σ_t and σ_y in all cases increase considerably with an increasing Mo concentration on account of the solid solution hardening regardless of heating temperature. These values of furnace cooling are somewhat low in the range with a smaller amount of Mo because of the precipitation of σ phase which is brittle, and are somewhat high in the range with a larger amount of Mo because of the precipitation of χ phase than those of water quenching⁽⁵⁾⁽⁶⁾. With an increasing Mo concentration, the E_l decreases gradually and then extremely when the alloys show two phases. The σ_t , σ_y and E_l become generally smaller with the rise in heating temperature because of the grain growth. In this alloy system, Co and Mo are both important alloying elements because these high damping alloys are usually used for the machine

members which are always subject to stresses and vibrations.

4. Pitting corrosion resistance

When the alloys with a passive film are used in the solutions which contain the halogen ion (Cl^-), pitting occurs from local destruction of the film. For the examination of the alloys' corrosion resistance, the pitting potential E_p is obtained by the chemical measurement of the anodic polarization curve in a NaCl solution. When the potential is reached, the current increases suddenly after the oscillations which are due to the repetition of pitting and passivation. In this investigation, the potential corresponding to the current density of 0.1 A/m^2 was used as the E_p . It is well-known that the binary alloys with Cr more than 13% are generally insoluble in NaCl and nitric acid solutions because of the formation of the passive film, but the corrosion resistance of these binary alloys is not adequate.

Figure 8 shows the effect of Mo concentration on the E_p for the same alloys as given in Fig. 4 furnace-cooled (a) or water-quenched

(b) after heating at 1273 K for 7.2 ks. In the figure, a dotted line of 1050 mV is the value of E_p at which point the pitting does not entirely occur. The E_p in all cases increases sharply with an increasing Mo concentration, and the pitting in the alloys with Mo more than 5% does not occur regardless of the heat treatment. The values upon furnace cooling are generally lower than those upon water quenching because the Mo and Cr concentrations in the matrix are reduced by the precipitation of χ and σ phases. Furthermore, the larger the Co, Mo and Cr concentrations, the better the pitting corrosion resistance⁽⁵⁾⁽⁶⁾. However, the optimum range with high- Q_{max}^{-1} and E_p in the furnace-cooled state consists of the composition with Co of 2–4%, Mo more than 1% and Cr of 15–25%, while the optimum range in the water-quenched state consists of the composition with Co of 2–6%, Mo more than 1% and Cr of 15–25%. For example, the pitting corrosion resistance of Fe–4%Co–2%Mo–20%Cr alloy is better than SUS 304 steel because the E_p values are 0.57 V and 0.34 V when water-quenched from 1273 K.

Fig. 8 Pitting potential E_p as a function of Mo concentration in Fe–Co–Mo–Cr alloys containing 4% Co and 20% Cr: (a) furnace-cooled and (b) water-quenched after heating at 1273 K for 7.2 ks.

5. Sulfuric acid corrosion resistance

The anodic polarization curve in H_2SO_4 solution shows that the current in the active range increases with rising potential and reaches a maximum. It then decreases suddenly with the beginning of passivation. The passive current of the alloys with high sulfuric acid corrosion resistance is very small. The current further increases in potential due to a solution of Cr, then its increment becomes violently increased due to the oxygen evolution in the trans passivity. Therefore, the alloys in the ordinary environments corresponding to their respective passivity have a high corrosion resistance, while those in the environments having very strong oxidation correspond to the trans passivity have a low corrosion resistance. Here, as the critical current density for passivation I_c and the passive current density I_p decrease, the capacity to resist sulfuric acid corrosion increase because the passivation occurs easily.

While the sulfuric acid corrosion resistance of binary Fe–Cr alloys is known to decrease

Fig. 9 Critical current for passivation I_c as a function of Mo concentration in Fe-Co-Mo-Cr alloys containing 4% Co and 20% Cr: (a) furnace-cooled and (b) water-quenched after heating at 1273 K for 7.2 ks.

with increasing Cr concentration, the quaternary Fe-Co-Mo-Cr alloys are improved in the corrosion resistivity with increasing Co and Mo concentrations.

For instance, Fig. 9 represents the effect of Mo concentration on the I_c of the same alloys as given in Fig. 4, when furnace-cooled (a) or water-quenched (b) after heating at 1273 K for 7.2 ks. By the Mo addition, I_c decreases sharply and passivation occurs easily. Here, it is due to the precipitations of σ and χ phases that the values of I_c upon furnace cooling are larger than those upon water quenching. However, the sulfuric acid corrosion resistance of the Fe-Co-Mo-Cr alloys is better. For example, the I_c of Fe-4%Co-2%Mo-20%Cr alloy is 26.9 A/m² which is smaller than 34.9 A/m² of SUS 304 steel in the water-quenched state.

According to the above experimental results on the quaternary Fe-Co-Mo-Cr alloys, the compositions with a high damping capacity and excellent properties consist of 2–4.5%Co, Mo less than 2.5%, 17–25%Cr and the rest Fe upon furnace cooling; and Co less than 6.5%, Mo less than 9.5%, 15–25%Cr and rest Fe

upon water quenching. However, the prices of the metals are high in the increasing order of Mo, Co and Cr, and the production of the alloys becomes more difficult with the increase of these alloying elements. Therefore, the optimum composition range is 2–4%Co, 1–3%Mo, 17–21%Cr and the rest Fe. The quaternary Fe-Co-Mo-Cr alloys are suitable as a damping material with high corrosion resistance under various environments because the alloys are superior to SUS 304 steel whose damping capacity is very low. The authors will be investigating the effect of additional elements so that we may improve these properties in the future.

IV. Conclusion

The internal friction, magnetic and mechanical properties and anodic polarization curves in 3% NaCl and 5% H₂SO₄ solutions were measured for quaternary Fe-Co-Mo-Cr alloys furnace-cooled, air-quenched and water-quenched after heating at 1173, 1273 and 1373 K for 7.2 ks, respectively. The results are summarized as follows:

(1) The maximum value of internal friction $Q_{\max}^{-1}$ of Fe-Co-Mo-Cr alloys is determined by the microstructures brought about by different alloying compositions and heat treatments. For the Fe-Co-Mo-Cr alloys containing 20%Cr, fairly high values of $Q_{\max}^{-1}$ upon furnace cooling is obtained in the composition range of 2–4.5%Co and less than 2.5%Mo, while those upon water quenching are obtained in the composition range of less than 6.5%Co and 9.5%Mo respectively.

(2) The alloys with high values of $Q_{\max}^{-1}$ show the α single phase and have moderately small H_c , whereas those with very low values of $Q_{\max}^{-1}$ show two phases and have very large H_c . Therefore, the $Q_{\max}^{-1}$ is higher when the magnetic induction and the magnetic hysteresis loss become larger at a small strain amplitude due to the irreversibility of magnetization.

(3) On account of the solid solution hardening, the tensile strength σ_t and the yield strength σ_y of the Fe-Co-Mo-Cr alloys containing 4%Co and 20%Cr increase with in-

creasing Mo concentration, but the elongation E_l decreases gradually. Furthermore, the increment in σ_t and σ_y and the decrement in E_l are large when the χ phase precipitates in the matrix of α the phase.

(4) The corrosion resistance to pitting and sulfuric acid in the Fe-Co-Mo-Cr alloys containing 4%Co and 20%Cr becomes higher with increasing Mo concentration because the pitting potential E_p increases sharply and the critical current density for passivation I_c decreases rapidly.

(5) In the quaternary Fe-Co-Mo-Cr alloys, the damping capacity is higher and the corrosion resistance to pitting and sulfuric acid is better. For example, the Fe-4%Co-2%Mo-20%Cr alloy water-quenched from 1273 K shows the E_p of 0.53 V and I_c of 26.9 A/m², whereas SUS 304 steel shows 0.34 V and 34.9 A/m². Therefore, the quaternary alloys are suitable as a damping material with a high corrosion resistance.

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