Effects of Cr content on the corrosion behavior of porous Ni–Cr–Mo–Cu alloys in H₃PO₄ solution

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1. Introduction

Owing to their good mechanical properties, high tensile strength, long fatigue life, and high-temperature creep resistance, Ni-based alloys have been widely applied to industrial sectors, including aviation and aerospace, seafaring, nuke industry, and power generation industries [1–4]. Their prosperous corrosion and oxidation resistance in acid and alkali environment makes them important materials [5, 6] in harsh environments.

Membrane separation is an efficient, quick, and energy-saving separation technique, which has been widely employed in the chemical industry, metallurgy, medical treatment, and environmental [7, 8] protection. Over the past decade, increasing literatures have shown that Ni-based porous alloys have superior oxidation and corrosion resistance [9, 10]. Ni-based porous alloys used as membrane separation materials in harsh environments have attracted much attention owing to their special performance, which make them latent candidates for various applications [11]. For example, Linping Yu [12] investigated the corrosion behavior of porous Ni–Cu alloys prepared by blended metal elemental powders reaction synthesis in a 0.01 mol l⁻¹ HF solution. The results revealed that compared with porous pure Ni, the alloy has excellent corrosion resistance in HF solution, and Rcorr value was 1847 Ω·cm². M V Cardoso et al [13] studied the corrosion resistance of Ni–Cr–Fe alloy in 0.5 mol l⁻¹ sodium sulphate solutions, the results revealed that Ni-
Cr-Fe alloys showed excellent corrosion resistance, and the passivation film was mainly composed of Cr oxides. At present, the research on corrosion resistance mainly focuses on nickel-based binary alloys and nickel-based ternary alloys. However, there are few reports about the corrosion resistance of nickel-based quaternary alloys. The previous work of our research group has proved that porous Ni–Cr–Mo–Cu alloy has excellent corrosion resistance in 10 wt% sulfuric acid [14], and its corrosion resistance in other acidic solutions should be further explored.

In this paper, the variation of the corrosion behavior of porous Ni–Cr–Mo–Cu with the chromium contents from 10 to 30 wt% in 30 wt% H₃PO₄ solution was investigated. This paper devotes to clarify the influences of chromium content on the corrosion behavior during immersion weight loss and electrochemical experiment via systematically comparing the corrosion characteristics of porous alloys. Strengthening research on these porous alloys is expected to solve the problems of short service life and high replacement cost of the core components of filter presses used in wet-process H₃PO₄ and hydrometallurgy.

2. Material and methods

2.1. Fabrication and characterization of the samples

The porous Ni–Cr–Mo–Cu were prepared via reaction synthesis of Ni, Cr, Mo, and Cu elemental mixed powders with all power size distribution of 38–74 μm, and the particle size of different alloying elements were displayed in figure 1. The composition of the alloys was (75 wt%-x)Ni(10 wt%+x)Cr10 wt%Mo5 wt%Cu (x = 0, 5 wt%, 10 wt%, 15 wt%, and 20 wt%, mass fraction). The electronic balance with a resolution of 0.01 g was taken to weigh the Ni, Cr, Mo and Cu powders with a designed size. And then, they were mixed in a mixer for 5 h with a speed of 200 r min⁻¹ at a ball/powder mass ratio of 5/1. The starting mixtures were cold-pressed into green compacts under 160 MPa with a dimension of 40 × 10 × 2 mm. The specimens were then sintered in a vacuum furnace under 2.0 × 10⁻³ Pa at the final temperature 1150 °C for two hours, after that, cooled to room temperature naturally. Pure Ni and Cu have the same specifications as these samples.
The fabricated alloys were characterized via XRD (Dmax 2500VB) to detect their compositions. Using the Archimedes method, the porosity of the various samples was measured; the formula is as follows:

\[ P = \frac{V_i - (M_i/\rho_1 + M_2/\rho_2 + M_3/\rho_3 + M_4/\rho_4)}{V_i} \times 100\% \]  

where \( P \) is the total porosity, \( V_i \) the total volume of the sample, and \( M_{1-4} \) and \( \rho_{1-4} \) are the masses and densities of Ni, Cr, Mo, and Cu, respectively.

### 2.2. Immersion weight loss experiment

The corrosion rate alteration of the porous Ni–Cr–Mo–Cu at room temperature with the chromium contents, from 10 to 30 wt%, was appraised via measuring the relative mass loss of the alloys versus time in 30 wt% \( \text{H}_3\text{PO}_4 \) solution. Distilled water was used to clean the specimens for 30 min via ultrasonic method, and the distilled water was changed every 5 min to ensure completely cleaned samples. Before transferring to the next step, the pH of the cleaned water used for cleaning in the last beaker was measured by a pH meter. If pH equals to \(~7\), then the samples were cleaned in ethanol (99.7 wt% pure) for 5 min, otherwise repeating the above-mentioned procedure till pH equals to \(~7\). The samples were dried in a vacuum drying oven at 80°C for 60 min, and then weighed on the analytical balance with an accuracy of 0.0001 g. The relative mass loss is used to indicate the corrosion attack. The morphologies of these porous alloy electrodes before and after the immersion test were characterized via SEM (FEI Nova Nano 230).

### 2.3. Electrochemical tests

All the electrochemical measurements were put into execution by using the criteria three-electrode system (CHI660E). The working electrode was porous Ni–Cr–Mo–Cu with a working area of 1.0 cm\(^2\). The thin Pt sheet with the same superficial area was counter electrode, and the reference electrical terminal was Ag/AgCl (in 3 M KCl solution) electrode. The test electrolyte was 30 wt% \( \text{H}_3\text{PO}_4 \) solution (general analytical reagents).

The potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) experiments were brought into effect after 10 h of immersion at an open circuit. Each electrochemical test was repeated three time. The corrosion current density and corrosion potential were acquired by Tafel approximation. The EIS measurements were made by polarization in the frequency range of \( 10^3 \text{ Hz} \) to \( 10^{-2} \text{ Hz} \) and 7 points measuring per decade. And Zview2.0 was used to define the EIS spectra.

### 3. Results and discussion

#### 3.1. Characterization of the samples

In this work, all sintered porous alloys samples with diverse chromium contents were characterized through XRD to confirm their phase compositions, which are depicted in figure 2. The alloys showed no apparent diffraction peaks corresponding to Mo, suggesting they have an amorphous alloy structure [15, 16]. The products of three peaks at 44.4°, 51.6°, and 76° in the diffraction spectra corresponding to NiCu, Cr\(_{1.12}\)Ni\(_{2.88}\) and Ni, respectively. According to our earlier report, as the chromium content increased, the peak intensities became higher, showing that more chromium reacted with nickel to form Cr\(_{1.12}\)Ni\(_{2.88}\), and the alloying degree increased with chromium proportion [14]. It can be seen from figure 2(b) that with the increase of Cr content, the two diffraction peaks show a regular left shift. In the formation process of porous materials, with the increase of Cr content, the diffusion ability of Cr atoms and vacancies is improved, and the solute can be dissolved into the matrix faster and more easily, resulting in the shift of material peak.

The porosity of the porous samples is displayed in figure 3. With the chromium content increased, the porosity rose, varying from 41.40 wt% to 48.36 wt%. This is consistent with previous studies, which reported that the porosity of sintered porous alloys test specimen vary with the chromium content [15]. In addition, the data of diffusion rates in different metal elements are listed in table 1. It can be seen that the diffusion rate of Cr atoms in Cu atoms is the largest, reaching \( 8.22 \times 10^{-13} \text{ m}^2 \cdot \text{s}^{-1} \) at 1150°C. This is due to the fact that Cu changes from solid to liquid, and the diffusion rate of solid-liquid is faster than that of solid-solid. The diffusion rate of Cr atoms in Cu atoms is followed by the diffusion of Cr atoms in Ni atoms at the diffusion rate of \( 1.61 \times 10^{-14} \text{ m}^2 \cdot \text{s}^{-1} \). Cr atoms play an important role in the formation of pores, which will migrate around Ni and Cu atoms to increase their volume, resulting in macroscopic volume expansion of the porous alloy. At the same time, pores will be formed in situ of Cr atoms due to the diffusion and migration of Cr.

Figure 4 shows the pore structure morphology of samples with different Cr contents. As displayed in this figure, the black parts are pores and the silver part is Ni–Cr–Mo–Cu alloy. It can be also seen from the figure that the pore structures with different Cr contents are different significantly. When the Cr content is 10 wt%, the
Figure 2. XRD patterns of porous Ni–Cr–Mo–Cu alloys prepared with different Cr contents and different range of 2θ: (a) 5 ∼ 80°; (b) 40 ∼ 60°.

Figure 3. Porosity of porous Ni–Cr–Mo–Cu alloys at different Cr content.
number and the average pore diameter of pores is small relatively. As the Cr content reaches 30 wt%, the number and the pore size of pores increases obviously, and the pores are interconnected gradually.

3.2. Immersion test

The changes in the mass of the alloys after immersion tests in 30 wt% H₃PO₄ solution, for 50 days are shown in figure 5. In 30 wt% H₃PO₄ solution, the percentage mass loss for the dense Ni and Cu were 1.64 wt% and 3.58 wt%, respectively, and those of the porous materials with the Cr content of 10 wt% and 30 wt% were 0.0651 wt% and 0.32 wt%, respectively. It shows that the sintered porous alloys samples displayed excellent anti-acid corrosion resistance and the sintered porous Ni–Cr–Mo–Cu sample at 30 wt% chromium content had better corrosion resistance in the H₃PO₄ solution. The results display that these sintered porous samples alloys possess better general erosion protection resistance than dense pure Ni in acid solutions.

The SEM images of the as-prepared sintered porous alloy sample at 30 wt% chromium content in 30 wt% H₃PO₄ solution are displayed in figure 6(a). The surface of the porous alloy is smooth, the pore structure is obvious and the pores are tightly connected, indicating that the alloying process of these samples has been completed (figure 6(a)). In the H₃PO₄ solution, the sintered porous sample at 30 wt% chromium content retained its smooth surface after corrosion (figure 6(b)).

| Diffusion element | Base element | $D_0/10^{-4}$ (m² s⁻¹) | $Q$ (kJ mol⁻¹) | $T/K$ | Diffusion rate/(m² s⁻¹) |
|-------------------|--------------|------------------------|----------------|--------|------------------------|
| Cr Ni 8.52 | 292.1 | 1423 | $1.61 \times 10^{-14}$ |
| Cr Mo 1.88 | 339 | 1423 | $6.76 \times 10^{-17}$ |
| Cr Cu 0.337 | 195 | 1338 | $8.22 \times 10^{-17}$ |
| Mo Ni 1.3 | 283 | 1423 | $5.31 \times 10^{-15}$ |
| Mo Cr 0.00027 | 242.8 | 1423 | $3.30 \times 10^{-17}$ |
| Cu Ni 0.61 | 255 | 1423 | $5.21 \times 10^{-15}$ |
3.3. Electrochemical measurements

3.3.1. Electrochemical impedance spectroscopy

EIS is a linchpin technique for evaluating corrosion resistance and apprehending the property of oxide-layer formation in an application-specific corrosive medium.

The impedance spectra of the sintered porous samples electrodes at different chromium contents and different voltages (versus open-circuit potential) after immersion in 30 wt% H₃PO₄ solution are displayed in figures 7 and 8. As can be seen from Nyquist plots (figure 7(a)), it is clear that the differences of Cr content significantly affects the semicircle diameter and the diameters of semicircular curves become large with the increasing of Cr content. The Nyquist plots include semicircular curves centered below the x-axis. This feature is helpful for interpreting charge transfer on irregular surfaces and the addition of Cr would improve the corrosion behavior. The capacitance behavior represented by the phase angle close to the maximum angle is typical of passivation materials and occurs in the low-mid and low-frequency range (figure 7(b)), which means that a passivation film is formed on all samples in the electrolyte. Besides, a large phase angle peak can indicate the interaction of at least two time constants. As shown in figure 7(c), an equivalent circuit is proposed to simulate the EIS data from the specimens, which is to explain the corrosion resistance behavior of porous Ni–Cr–Mo–Cu alloys electrodes. To explain corrosion resistance behavior of the samples electrodes, an equivalent circuit is put forward to simulate the EIS data acquired from the samples, as displayed in figure 7(d). The electrical equivalent circuit consists of the solution resistance ($R_s$), which is connected to a pair of resistive and capacitive components. Besides, $R_2$ is the additional resistance of the solution inside the pores, $R_3$ is the charge transfer resistance of the oxygen layer, $C_p$ is the capacitance of the pore wall and CPE is the capacitance of the oxygen layer [17]. Notably, the equivalent circuit used in the model was not so ideal to reflect the actual situation. So, the capacitor in the circuit was supplanted by a constant-phase element (CPE) to remedy the inhomogeneity of the
The data obtained from the EIS test after fitting to the equivalent circuit are listed in Table 2. It is clear to see that all the $R$ values rise with the increase of Cr content. It means that the samples with higher Cr content have better corrosion resistance. In addition, as displayed in this figure, the samples with different Cr contents have similar electrochemical properties in phosphoric acid solution. This is due to the fact that the active PO$_4^{3-}$ will easily adsorb on the surface of porous metal and first occupy the active sites on the surface, thereby accelerating the dissolution of metal atoms. As shown in the Table 2, the value of CPE almost unchanged, suggesting that the quantity of adsorbed species on the surface of porous Ni–Cr–Mo–Cu alloys depended on the concentration of PO$_4^{3-}$. So, under the same tested concentration, the samples with different Cr contents exhibited the same corrosion impedance behavior [12].

The relationship of porous Ni–30 wt%Cr–10 wt%Mo–5 wt%Cu alloy with corrosion resistances and different voltages (versus open circuit potential) were performed due to the best corrosion resistance ability. The data was processed by above method. And the Nyquist, Bode and equivalent circuit are displayed in Figure 8, the data obtained from the EIS test after fitting to the equivalent circuit are also listed in Table 3. It is evident that the $R$ values decrease with the increase of voltages, it means that the samples exhibits good corrosion resistance at open circuit potential. Besides, $R_s$ values are all very small with different voltages, which means that the diffusion process was weak and not the nominate step.

Contrary to the samples, the Nyquist plot of the impedance for the dense Ni only shows one capacitive loop; the high-frequency impedance loop did not arise because it is related to the pore texture. Otherwise, the $R_3$ value remarkably increased from 432 to 1123 $\Omega$·cm$^{-2}$ accompanying the chromium content progressive increment from 10 to 30 wt% in 30 wt% H$_3$PO$_4$ solution at a temperature of 20 °C (Table 2), which manifests that the corrosion resistance of the samples increased with rising chromium content. This result is brought into correspondence with those of the immersion tests (Figure 5). The corrosion resistance of the samples is attributed to the uniformity chemical constituent of the pore structures. As Yu previously reported [12], during the heating processes, the randomly settled metal elemental particles throughout the primal powder mixture gradually diffuse in heated environments, and the local compact regions still contain the correct atomic
percentage of the elements in the step elevated sintering process. Sufficient diffusion between different metal elemental powders as well as adequate heating and holding time gives rise to phase homogenization in the test specimens. Hence, the whole porous skeleton becomes equipotential, and the pore wall exposed to an acid solution can certainly be considered as an equipotential surface, which is mainly in charge of the excellent corrosion resistance of the test specimens, similar to pure Ni, in acid solutions [12].

3.3.2. Polarization test
The corrosion current density ($J_{\text{corr}}$) was determined via extrapolating the cathode polarization curves and linear Tafel segments of the anode [20], and the $J_{\text{corr}}$ values can reflect the corrosion rate more accurately than the free corrosion potential ($\varphi_{\text{corr}}$) [21]. Besides, a material with high corrosion current density, low corrosion potential, and high polarization resistance ($R_p$) would exhibit a high tendency to oxidization and corrosion.

Table 2. Fitting results of EIS measurements at various chromium content on the investigated porous Ni–Cr–Mo–Cu in $\text{H}_3\text{PO}_4$ solution.

| Porous Ni–Cr–Mo–Cu | Cr content (wt%) |
|---------------------|-----------------|
|                     | 10   | 15   | 20   | 25   | 30   | Dense Ni   |
| $R_1$ (Ω)           | 2.813 | 2.827 | 2.839 | 2.804 | 2.847 | 1.823      |
| $C_1$ (mF)          | $4.27 \times 10^{-5}$ | $4.36 \times 10^{-5}$ | $4.42 \times 10^{-5}$ | $4.47 \times 10^{-5}$ | $4.43 \times 10^{-5}$ | $8.84 \times 10^{-7}$ |
| $R_2$ (Ω)           | 1.998 | 1.951 | 1.892 | 1.495 | 1.854 | 0.60933    |
| $CPE_1-T$           | 0.01275 | 0.012779 | 0.012726 | 0.012581 | 0.011032 | 0.000421   |
| $CPE_1-P$           | 0.65148 | 0.65199 | 0.65475 | 0.66083 | 0.71197 | 0.81663    |
| $R_3$ (Ω)           | 432   | 497   | 573.6 | 629   | 1123  | 98.55      |

Figure 8. Nyquist plots and bode plots of porous Ni–30wt%Cr–10 wt%Mo–5 wt%Cu alloy at different upon open circuit potential (versus OCP) in $\text{H}_3\text{PO}_4$ solution: (a) Nyquist plots; (b) $\lg Z$ versus $\lg f$; (c) phase angle versus $\lg f$; (d) Equivalent circuit.
Figure 9 shows the electrochemical polarization plots of the specimens at chromium content of 30 wt% in different temperatures (30 °C–70 °C). And the alloy exhibited the best corrosion resistance in 30 wt% H₃PO₄ solution. As shown in table 4, some fitting electrochemical parameters are generalized in detail. Stable
passivation regions on the polarization curve was observed in the H₃PO₄ solution for all the temperatures. The anode polarization curves of the sample reflect the corrosion active dissolution at all concentrations, and the corrosion current density ($J_{\text{corr}}$) of the specimen was enhanced as the test temperature increased.

The activation energy of the corrosion process can be derived using the following equation [22]:

$$\log J_0 = \log A - \frac{E_a}{2.303R \cdot T}$$

wherein $T$, $A$, $R$ and $E_a$ are the absolute temperature, Arrhenius preexponential constant, gas constant and apparent corrosion activation energy, respectively. Clearly, When the chromium content was higher, the corrosion activation energy was much higher. The corrosion process activation energy was much higher at higher chromium contents. This suggests that the Cr₂O₃ and MoOₓ ($x = 1, 2, 3$) films formed on the surface of the electrodes protected them from corrosion, reducing the corrosion rate in 30 wt% H₃PO₄ solution.

The stabilization of the sintered porous alloy specimens under harsh operating conditions was further evaluated using the open-circuit potential ($E_{\text{ocp}}$) of the electrodes to authenticate their stability in the acid solution. Because it is an important parameter to make an appraisal on the corrosion characteristics of these materials, the $E_{\text{ocp}}$ of the porous electrodes was also measured as a functionality of testing duration. Figure 10 shows $E_{\text{ocp}}$ as an efficacy of time for the specimens from 10 to 30 wt% (with 10 increments) chromium content in the H₃PO₄ solution. From the figure, the open circuit potential of porous Ni–Cr–Mo–Cu changes sharply and tends to be stable in a relatively short time. This shift indicates the passivity on electrode surface. It is well known that the material exhibits higher positive and it has better corrosion resistance. Herein, the porous Ni–Cr–Mo–Cu with a higher Cr content shows a higher positive potential, which shows that the sample with a higher Cr content has better corrosion resistance.

### 3.4. XPS

The chemical valences of the elements in the sintered porous alloys samples were defined via XPS analysis. Figure 11(a) displays the XPS spectra for the passive films formed on the superificies of the test specimen electrodes after immersion tests in 30 wt% H₃PO₄ solutions. Nickel, chromium, and molybdenum were present.
in the original sample in the metallic forms. The Cu signal deconvolution showed that the component of Cu was monovalent, Cu (0) (932.43 eV) being the most important chemical valence, which indicates that copper basically maintains its original valence during the corrosion process.

As could be seen in figure 11(b), the narrow scanning spectrum of Ni-2p can be resolved into four doublet peaks, which are allocated to the oxidation valence states of Ni, Ni^{2+}, and Ni^{4+}, matching Ni, NiO, and Ni_{4}P_{4}, respectively. Quantitative assay of XPS indicates that a greater percentage of nickel (50.2 wt%) was in the form of NiO (Ni^{2+}), 37.0 wt% as Ni, and the rest was in Ni_{4}P_{4} (Ni^{4+}). This result agrees well with the early report, where NiO was mass dominant role in the passive oxide layers on Ni alloys. Apropos of Cr-2p (figure 11(c)), the peak is situated at 574.72, 577.42, 583.73, and 586.92 eV, and the corresponding substances are Cr, Cr_{2}O_{3}, Cr, and HCrO_{2}, respectively. Quantitative analysis by XPS revealed that the most important valence state of chromium (37.2 wt%) was in the form of HCrO_{2} (Cr^{3+}), 29.1 wt% as Cr_{2}O_{3} (Cr^{3+}), and the rest in Cr state. The surface passivation layer of the sintered porous alloy sample contained major dense Cr_{2}O_{3}, which could promote the stability of the passivation layer. The XPS results are consistent with those of the immersion test. Figure 11(d)

Figure 11. XPS spectra of porous Ni–Cr–Mo–Cu alloys after corrosion tests in H_{3}PO_{4} solution: wide scan, Ni-2p, Cr-2p, Mo-3d, and Cu-2p (a)–(e), respectively.
displays the narrow scanning spectrum of Mo-3d spectra, which can be allocated to three peaks located at 228.36, 232.20, and 235.48 eV, which correspond to MoO, MoO₂, and MoO₃, respectively. As exhibited in figure 11(e), the peak of Cu-2p can be decomposed to mainly two peaks: the principal peak located at 932.53 eV and the subsidiary peak at 952.20 eV, corresponding to Cu and CuO, respectively.

The XPS spectra show that nickel and chromium elements in the sintered porous alloys samples were in the zero-valance states after the immersion test. We believe that Ni–Cr alloy was formed during the sintering process and it can resist corrosion of H₃PO₄ solution effectively. Research has confirmed that Ni–Cr alloy exhibited excellent corrosion resistance in most acid solutions including the H₃PO₄ solution [23]. Therefore, Ni-Cr alloy is very important for corrosion resistance in H₃PO₄ solution. A continuous elevation in the chromium content was beneficial to the formation of dense Cr₂O₃ films, which reduced the solid-solution content of Cu in the Ni–Cr alloy, thereby improving the anti-acid erode resistance of the sintered porous alloys samples. This occurred according to the following reaction [24]:

\[
2\text{Cr} + 3\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^-
\]

Additionally, according to the early report, the Mo-based oxide species on the appearance of the specimen enhanced the stability of the Cr₂O₃ passive film, and this proceeded according to the following chemical reaction [25]:

\[
\text{Mo} + 2\text{H}_2\text{O} \rightarrow \text{MoO}_2 + 4\text{H}^+ + 4\text{e}^-
\]

Further oxidation of the Mo-based oxide species to MoO₂ and trans-passivation of Cr passivated the damaged passive layer and enhanced the resistance of the alloy systems to pitting corrosion [26]. Because of the combination of Cr and Mo elements, the sintered porous alloy sample at 30 wt% chromium content exhibited better corrosion resistance in the H₃PO₄ solution. In addition, the increase in the porosity indicates an increase in specific surface area, which aids violent corrosion. In this study, the porosity of the samples with different Cr contents varied slightly. The effect of porosity on acid corrosion resistance of sintered porous alloy samples in H₃PO₄ solution is slight [12, 27].

4. Conclusions

Porous Ni–Cr–Mo–Cu alloys with varied chromium proportion and copious, mutually anastomosis pores and approximately smooth pore walls were prepared via reactive synthesis sintering, and the porosity of the alloys increased with ascent of chromium content.

Immersion tests showed that the alloys presented prosperous corrosion resistance property, compared to dense Ni, in H₃PO₄. The corrosion rate of the alloys in H₃PO₄ solution decreased with rising chromium content owing to the formation of Ni–Cr alloys and the sedimentation of Mo oxide films.

The electrochemical analysis results show that the sample at 30 wt% chromium content demonstrated super corrosion resistance in the H₃PO₄ solution. At chromium content of 30 wt%, the charge transfer resistance and activation energy were 1123 Ω and 74.10 kJ mol⁻¹, respectively.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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