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Effects of Ag and Cu Additions on the Electrochemical Migration Susceptibility of Pb-free Solders in Na_2SO_4 Solution

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Abstract. The smaller size and higher integration of advanced electronic package systems result in severe electrochemical reliability issues in microelectronic packaging due to higher electric field under high temperature and humidity conditions. Under these harsh conditions, electronic components respond to applied voltages by electrochemical ionization of metal and the formation of a filament, which leads to short-circuit failure of an electronic component, which is termed electrochemical migration. This work aims to evaluate electrochemical migration susceptibility of the pure Sn, Sn-3.5Ag, Sn-3.0Ag-0.5Cu solder alloys in Na_2SO_4. The water drop test was performed to understand the failure mechanism in a pad patterned solder alloy. The polarization test and anodic dissolution test were performed, and ionic species and concentration were analyzed. Ag and Cu additions increased the time to failure of Pb-free solder in 0.001 wt% Na_2SO_4 solution at room temperature and the dendrite was mainly composed of Sn regardless of the solders. In the case of SnAg solders, when Ag and Cu added to the solders, Ag and Cu improved the passivation behavior and pitting corrosion resistance and formed inert intermetallic compounds and thus the dissolution of Ag and Cu was suppressed; only Sn was dissolved. If ionic species is mainly Sn ion, dissolution content than cathodic deposition efficiency will affect the composition of the dendrite. Therefore, Ag and Cu additions improve the electrochemical migration resistance of SnAg and SnAgCu solders.

Keywords *: electrochemical migration, SnAg and SnAgCu solders, time to failure, pitting corrosion*

1. Introduction

Migration behavior which induces the insulation breakdown in printed circuit board (PCB) can be divided into 3 kinds as follows; electrochemical migration, electromigration, and stress migration. Electrochemical migration can be affected by electric field under humidity and thus metals migrate on or beneath the surface of the medium. Electromigration means the atoms migrate by electron wind due to high current density. The void formed at the cathode and the hillock occurred at the anode. However, stress migration was induced by the stress in the medium and this is also called as a whisker.

The smaller size and higher integration of electronic components results in smaller gaps between metal conducting layer in an electronic package and PCB. Under high temperature and humidity, electronic components respond to applied voltages by electrochemically ionization of metals, and the formation of a conductive anode filament at the anode and dendrite at the cathode, which leads to short-circuit failure of an electronic component. This is known as electrochemical migration. [1)-3)] The migration of Ag, Cu, Sn, and SnPb refers to the phenomena in which metals migrate on or beneath the surface of metallic thin films, electro-plating, colloid metals or conductive coating materials under an applied current or voltage in high humidity or moist conditions. These phenomena can induce the fatal destruction and breakdown of the system of connection between electric circuits. Thus, this migration is becoming an increasingly important issue, because electronic components are becoming smaller and the distance between the electric circuits is decreasing.

Ag migration on the telephone-switchboard was reported for the first times by Kohman *et al.*[4)] They showed that electric field and water were needed for the migration and the migration occurred by the electrochemical process. Also, it was reported that any migration was occurred at short time or very low electric field, and thereafter it has

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been reported for the metals such as Cu, Sn and Au.[4),5)] When the water or moisture adsorption occurs at the metal electrode, metals ionized metallic ions at the anode and $H_2O \rightarrow H^+ + OH^-$ reaction took place at the cathode. By the electric field, the dendrites grow from the cathode to the anode.

In the respect of environmental and health concerns, to respond to these issues, the development of lead-free solder is required in electronic assembly. Sn-based solder alloys with addition of one or more metals like Ag, Cu, Bi, Zn, In and Sb have been actively investigated. The SnAg and SnAgCu solder alloys become to be commercial one in these solders. However, standard electrode potentials of alloying elements are Sn=-0.138V(SHE), Ag=+0.779V(SHE), Cu=+0.342V (SHE), respectively.[8)] This potential difference between alloying elements may affect the electrochemical migration susceptibility of Pb-free solder alloys.

H. Tanaka reported[9)] that the intermetallic compound (Ag_3Sn) phase was formed in the SnAg solder as a product of the reaction between Sn and Ag, and Ag_3Sn phase dispersed throughout the Sn component. In the SnCu solder, the intermetallic compound (Cu_xSn_y) phase was formed from Sn and Cu, and Cu_6Sn_5 phase minutely dispersed throughout the Sn component. Ag and Cu, which combine with Sn to form stable intermetallic compounds that do not dissolve, and so the migration-resistant characteristics of Sn-3.5Ag and Sn-0.8Cu are related to the dissolution characteristics of Sn. They also reported that these Pb-free solders have higher resistance to migration than conventional leaded solder because Sn forms a more stable passivity film than Pb.[9)] According to D. Q. Yu *et al*.,[10)] for Sn-Ag and Sn-Ag-Cu solders, the dendrites were mainly composed of Sn. In the solders of Sn-Ag and Sn-Ag-Cu, the Ag element formed intermetallic compound Ag_3Sn with Sn. Ag is difficult to escape from the compound and the migration is prevented. The same situation of Cu in the solder, they turn to Cu_6Sn_5 compounds in the solder. To Cu containing solders, Cu content is very small in the compositions of dendrite.[10)] On the other hand, it was well-known that Ag was one of the most susceptible metals to migration.[11)]

According to T. Takemoto et al.,[12)] the important factors for the susceptibility of solder alloys to electrochemical migration in pure water, using the glass slide method, can be summarized as follows; (1) the high dissolution rate of the metal as ionic species, (2) the low rate of hydrogen evolution at the cathode and (3) the low saturation concentration of metallic ions in pure water. Sn was found to have superior electrochemical migration resistance to Pb and Sn-Pb alloys. This behavior corresponds well with the corrosion susceptibility of Sn, Pb and their alloys in pure water.[13)] Our group has reported a new mechanism on the electrochemical migration behavior of SnPb solder alloys;[6),7)] when pH of test solution is high, Pb tends to deposit easily than Sn deposition, but Sn tends to precipitate easily when pH of test solution is acidic. We proposed that the deposition efficiency of Pb is higher than that of Sn.[6)]

This work aims to evaluate the effects of Ag and Cu on the electrochemical migration susceptibility of Pb-free solders in Na_2SO_4 solution.

2. Experimental procedure

2.1 Water drop test (WDT)

To evaluate the resistance to electrochemical migration, we used the WDT. The specimen used for the WDT was made on a Si wafer substrate. On the Si wafer substrate, a Ni under bump metallurgy (UBM) layer was sputtered (to a thickness of 3000 Å). A pad with a 300 μm space pattern was made by using the photo-resist and screen printing methods. Solder pastes were reflowed on the Ni UBM in a reflow oven. The WDT was performed to understand the failure mechanism in the pad patterned solder alloy in Na_2SO_4 solution at room temperature. We dropped 2 μl of the test solution between the pad patterned solders with a microsyringe and then applied a DC voltage of 2 V by using a potentiostat (EG&G, model 273A). The current was measured and continuous images of the migration process were recorded with a video-microscope.

2.2 Polarization test

The specimen used for the polarization test was made on a Ni-electroplated copper plate, which plate was cut into 1 cm×1 cm specimens. The solder pastes were reflowed. After polishing the specimens with 0.05 μm of alumina paste, we connected a coated lead wire to the specimens and sealed the surface with epoxy resin (exposure area: 0.09 cm^2). Anodic and cathodic polarization tests were performed in deaerated Na_2SO_4 solution at 25 ℃ by using a potentiostat (Gamry, model DC105). The solution was deaerated with N_2 gas for 30 min at 100 ml/min. A saturated calomel electrode (SCE) was used as a reference electrode and a high-density graphite rod was used as a counter electrode. The scanning rate was 1 mV/s.

2.3 Anodic dissolution and ion analysis

To analyze the dissolved species and their concentration, we performed an anodic dissolution test and ion analysis.

The test specimens for the anodic dissolution test were made as follows: to prepare the UBM, we deposited Ni thin film on a Cu substrate by electroplating; we then reflowed the SnPb solder on the Ni UBM in a reflow oven. The anodic dissolution test was performed by using a potentiostat (Gamry, model DC105) in deaerated Na_2SO_4 solution at room temperature. A dissolution potential was applied to the specimen for 1 h and obtained the anolyte. We used an ICP/AES (Spectro, model Flame Modula S) to analyze the ionic species and concentration.

2.4 Surface analysis

After the WDT, the pad patterned specimens were allowed to dry naturally and then the specimen was transferred to a SEM chamber. The images and composition of the pad and dendrite were observed using SEM-EDS (JEOL, model JSM-6300).

3. Results and discusstion

Representative commercial Pb-free solders are SnAg and SnAgCu, SnBi, SnZn alloys and so on. In this work, SnAg alloys were used and the effects of Ag and Cu on electrochemical migration susceptibility were evaluated using an electrochemical technique. A pad with a 300 µm space pattern and 2 V were applied between the electrodes.

Fig. 1 shows the effects of Ag and Cu on the time to failure in 0.001 wt% Na_2SO_4 at room temperature by water-drop test. Time to failure was measured 3~5 times per solders and the tolerance range also revealed in the figure. Also, time to failure was defined as the time which the dendrite connected from the cathode to the anode after applying the voltage. As shown in figure, Ag increased the time to failure of pure Sn solder and Cu also increased the time to failure of SnAg solder.

Fig. 2 shows the image and composition analysis on the dendrites formed on Sn3Ag0.5Cu solder in 0.001 wt% Na_2SO_4 at room temperature. In Fig. 2(a), the left pad was the anode and the right pad was the cathode. This figure revealed that the dendrites grew from the cathode to the anode. However, dendrite morphology varies even the same environment. Fig. 2(b) represents the composition of the dendrites near the anode, middle region, and near the cathode. The composition was obtained by SEM-EDS analysis. The composition of the dendrite formed on SnAgCu solder was almost Sn, and Ag and Cu contents were trace under analysis limit(* in the figure means under this limit). Also, the main component was Sn in pure Sn solder and SnAg solder.

According to other results,[9] the intermetallic compound (Ag_3Sn) phase was formed in the SnAg solder as a product

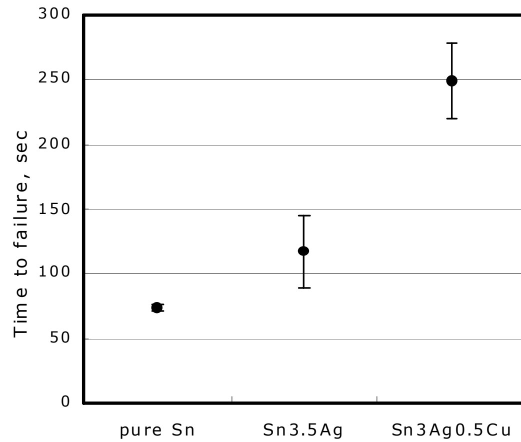
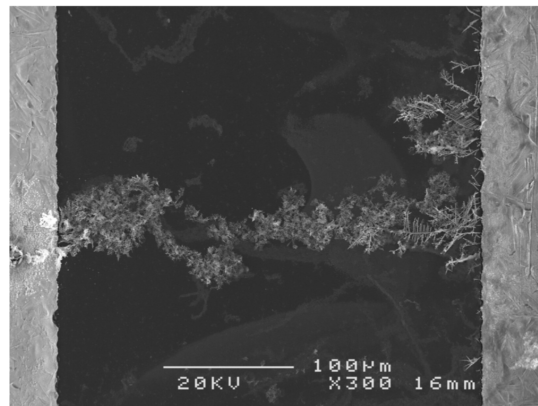
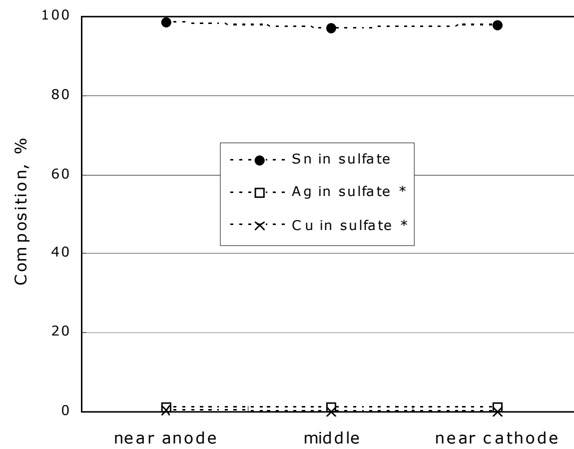


Fig. 1. Time to failure of pure Sn, Sn3.5Ag and Sn3Ag0.5Cu determined by the water-drop test at room temperature (applied voltage: 2 V) in 0.001wt% Na_2SO_4



(a)



(b)

Fig. 2. Dendrite composition formed on Sn3Ag0.5Cu solder by water drop test in 0.001 wt% Na_2SO_4; (a) SEM image, (b) composition of dendrite at each region

of the reaction between Sn and Ag, and Ag_3Sn phase dispersed throughout the Sn component. In SnCu solder, the intermetallic compound phase was formed from Sn and Cu, and Cu_6Sn_5 phase minutely dispersed throughout the Sn component. Ag and Cu, which have been shown to quickly lead to migration, both combine with Sn to form stable compounds that do not dissolve, and so the migration-resistant characteristics of Sn-3.5Ag and Sn-0.8Cu are related to the dissolution characteristics of Sn. As shown in Fig. 1, however, Ag and Cu additions in the solders could increase the electrochemical migration resistance in Na_2SO_4 solution and this means these elements may affect the resistance in addition to the formation of intermetallic compounds. Therefore, electrochemical technique was introduced.

In summary, electrochemical migration resistance in Na_2SO_4 solution was improved by the addition of Ag and Cu in the solders but the dendrite was mainly composed of Sn regardless of the solders. According to the H. Tanaka,[9] electrochemical migration resistance should be the same to pure Sn solder, but its resistance was different depending upon the solder composition.

Fig. 3 shows the anodic polarization curves obtained in deaerated 0.001 wt% Na_2SO_4 at 25 ℃ for pure Sn, Sn3.5Ag, and Sn3Ag0.5Cu solders. Corrosion potential was similar to each other and the passive film formed by anodic polarization and its passive current was also similar. However, in the case of pure Sn solder, pitting corrosion occurs at -47 mV(SCE), and in the case of Sn3.5Ag solder, transpassive current increased by pitting corrosion, but Sn3Ag0.5Cu solder showed the excellent passivity. Passivation mechanism by Ag and Cu will be described elsewhere.[14]

Fig. 4 shows the relation between time to failure and (a) corrosion potential and (b) pitting potential. Although Ag and Cu increased time to failure, corrosion potential remains constant. It means corrosion potential does not affect electrochemical migration susceptibility. However, as shown in Fig. 4(b), when pitting potential increases, time to failure improved. It means electrochemical migration resistance was closely related to the pitting corrosion resistance of the solders. When Ag and Cu added to the solders, Ag and Cu could form the intermetallic compounds with Sn.[9),10)] Generally, intermetallic compounds are noble and thus inert itself. Sometimes, intermetallic compounds degraded the matrix - typically, sigma phase in stainless steels. Many reports said that SnAg and SnAgCu solders showed good electrochemical migration resistance because of the formation of the intermetallic compounds.[9),10)] However, as shown in Fig. 3, Ag and Cu additions could improve the passivation behavior of the

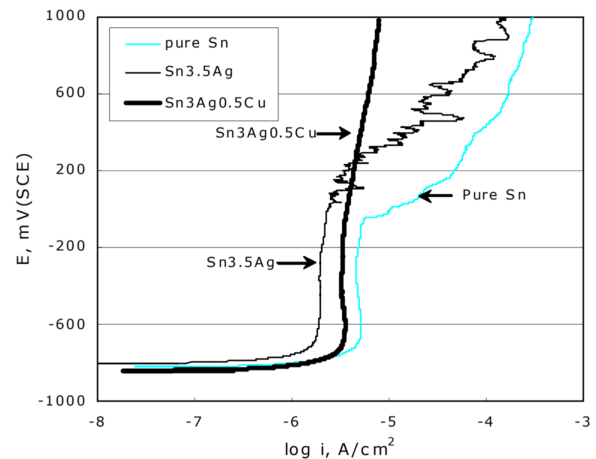
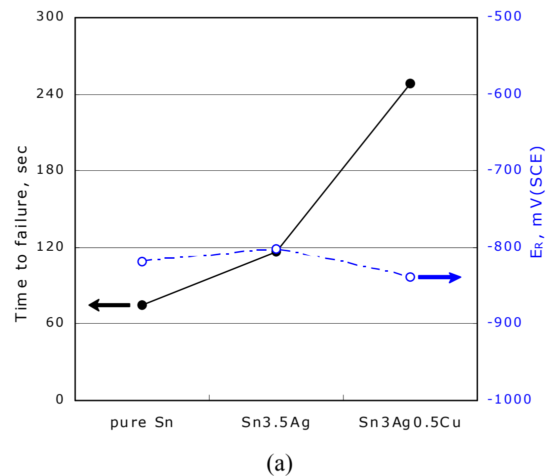
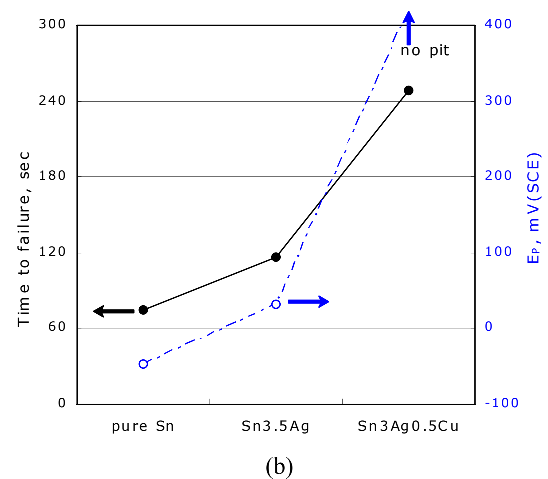


Fig. 3. Anodic polarization behavior of pure Sn, Sn3.5Ag and Sn3Ag0.5Cu in deaerated 0.001 wt% Na_2SO_4 at 25℃



(a)



(b)

Fig. 4. Effect of Ag, Cu of pure Sn, Sn3.5Ag and Sn3Ag0.5Cu at 25℃ in deaerated 0.001 wt% Na_2SO_4; (a) time to failure vs. corrosion potential, (b) time to failure vs. pitting potential

solders even though the formation of intermetallic compounds.

During a water drop test, applied voltage polarized the anode and cathode. Thus, anode potential and cathode potential were measured.[7] When 2 V applied, the anode potential was about 0 V(SCE) and the cathode potential was about -2 V(SCE) regardless of the solders and the corrosive environments. Fig. 5 shows the relation between time to failure and the anodic current density at 0 V(SCE) in anodic polarization curves of Fig. 3. When time to failure increased, anodic current density at 0 V(SCE) decreased. In other words, Ag and Cu additions reduced the anodic current density.

When any voltage applied to the electrodes under water adsorption, metals ionized from the anode and these metallic ions migrated through the water film or insulation materials and the filament formed and finally it breaks the insulation resistance. This is one of the electrochemical migration mechanisms.

As discussed the above, the addition of Ag and Cu to solders improved the passivity and the pitting corrosion resistance of the solders. The dendrite can grow from the reduction and deposition of metallic ions. Fig. 6 shows the relation between dissolved ions contents and time to failure. Dissolution was performed by applying the potential of 0 V(SCE) for 1 hour and the ions was analyzed using ICP/AES. As shown Fig. 6(a), when total dissolved ions decreased, time to failure increased. According to T. Takemoto *et al.*[12] the important factors for the susceptibility of solder alloys to electrochemical migration in pure water; (1) the high dissolution rate of the metal as ionic species, (2) the low rate of hydrogen evolution at the cathode and (3) the low saturation concentration of metallic ions in pure water, the effect of dissolved ions

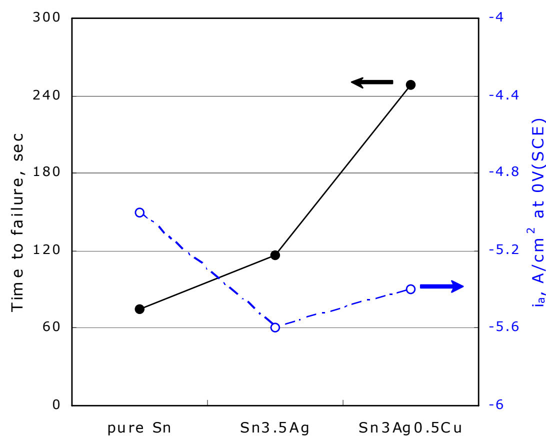
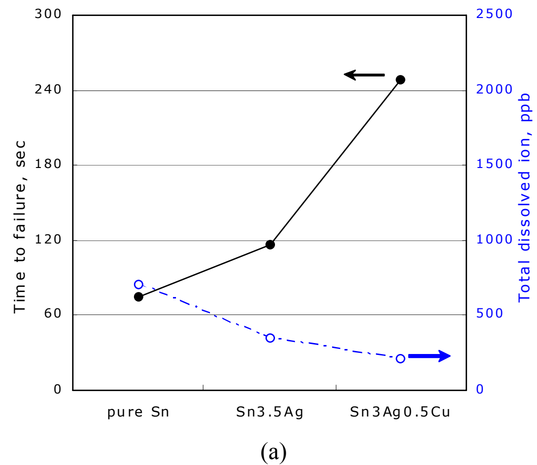
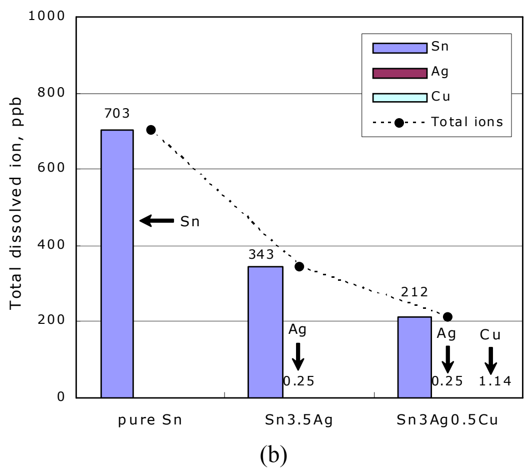


Fig. 5. Relation between time to failure and anodic current density at 0 V(SCE) in anodic polarization curves of Fig. 3



(a)



(b)

Fig. 6. Effect of Ag, Cu of pure Sn, Sn3.5Ag and Sn3Ag0.5Cu at 25℃ in deaerated 0.001 wt% Na_2SO_4; (a) time to failure and total dissolved ion, (b) total dissolved ion and dissolved ion of Sn, Ag, Cu

content was apparent. Dissolved species was almost Sn ion but Ag and Cu ions were very small as shown in Fig. 6(b). It is considered that Ag and Cu additions improved the passive film and reduced the dissolution of the solders.

The above result showed the composition of the dendrite formed on SnAg and SnAgCu solders was Sn and Ag/Cu additions improved the electrochemical migration resistance. Also, the composition of the dendrite formed on SnPb solders was mainly Pb mixed with Sn[6] and Pb addition also improved its resistance.[6),7] In the case of SnPb solders, even though dissolution content of Sn is larger than that of Pb, dendrite composition was mainly Pb. This behavior was due to the cathodic deposition efficiency of Pb ion among the dissolved ions. In the case of SnAg solders, when Ag and Cu added to the solders, Ag and Cu improved the passivation behavior and pitting corrosion resistance and formed inert intermetallic com-

pounds[9),10)] and thus the dissolution of Ag and Cu was suppressed; only Sn was dissolved. If ionic species is mainly Sn ion, dissolution content than cathodic deposition efficiency will affect the composition of the dendrite. Therefore, Ag and Cu additions improve the electrochemical migration resistance of SnAg and SnAgCu solders.

4. Conclusions

To evaluate the effects of Ag and Cu on the electrochemical migration susceptibility of Pb-free solders, water drop test, electrochemical approach, and solution analysis were performed.

(1) Ag and Cu additions increased the time to failure of Pb-free solder in 0.001 wt% Na_2SO_4 solution at room temperature and the dendrite was mainly composed of Sn regardless of the solders.

(2) In the case of SnAg solders, when Ag and Cu added to the solders, Ag and Cu improved the passivation behavior and pitting corrosion resistance and formed inert intermetallic compounds and thus the dissolution of Ag and Cu was suppressed; only Sn was dissolved. If ionic species is mainly Sn ion, dissolution content than cathodic deposition efficiency will affect the composition of the dendrite. Therefore, Ag and Cu additions improve the electrochemical migration resistance of SnAg and SnAgCu solders.

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