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Influence of Aluminium and Zinc Additives on the Physical and Thermal Behaviour of Cast Copper

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ABSTRACT. *Roles of aluminium and zinc additions on the physical and thermal behavior of cast copper are investigated. Metal casting is used in the production of bronze and brass with composition of 10wt% each Al and Zn. Cast alloys has been studied by subjecting to isochronal and isothermal ageing at various temperatures up to 500°C and different times ranging from 15 to 240 minutes respectively. Micro-hardness values of the differently processed alloys have been measured to understand the ageing behavior of Cu with Al and Zn addition. It is observed that hardening takes place due to solid-solution hardening. Al addition responses results to some age hardening behavior in the aged alloy due to formation of hard and brittle intermetallic copper aluminites. The thermal conductivity of the alloys increases marginally through heat treatment due to stress relieving and decreases due to formation of intermetallic precipitates. It is also found that incorporation of Al and Zn affects the absorbance properties of cast Cu. A microstructural study of the alloys reveals that the cast alloys contains the different phases of grains. It is also observed that all the alloys accomplish partially re-crystallized state after aging at 400°C for one hour.*

Keywords: Cu-alloys, Age hardening, Precipitates, Conductivity, Absorbance, Microstructure

1. INTRODUCTION

Copper and its alloys are a good number of adaptable engineering materials [1]. The grouping of properties like strength, conductivity, corrosion resistance, machinability and ductility creates copper appropriate for an extensive range of function [2, 3]. These properties can be supplementary improved with variations in composition and manufacturing methods. Copper can be strengthening by the various common methods like solid solution and work hardening, as well as dispersed particle and precipitation hardening. The usually used solid-solution hardening elements are zinc, nickel, manganese, aluminum, tin, and silicon, listed in approximate order of increasing effectiveness [4-6]. When aluminium is added to copper, it forms alloys known as aluminum bronze which is stronger and harder than the pure metals. Compositions vary, but most modern bronze is 88% copper and 12% Aluminium. Zinc addition with copper forms the brass alloys. Brass represents the entire range of available solid-solution compositions of each element: up to 35% Zn [7, 8]. Alloying elements increases or decreases the properties of a metal [9, 10]. The addition percentages also play an important role on the properties of that metal [11].

This paper presented the influence of alloying elements like Al and Zn in copper as ten weight percent of each alloying element was incorporated in copper. Straightforward binary alloys were chosen for this study to segregate the influence of individual alloying element on strengthening, thermal and microstructures behaviours of the alloys under different heat treatment.

2. MATERIALS AND METHODS

Commercially pure Cu, Cu-10Al and Cu-10Zn alloys were used in the current study. In the development of the alloys, the commercially pure copper, aluminium and zinc were taken. Melting was carried out in a clay-graphite crucible in a natural gas fired pit furnace under suitable flux cover. The final temperature of the melts was always maintained at 1300±15°C. A preheated steel mould (200°C) size of 20×100×150 in millimeter was prepared which was coated inside with a film of water-clay. The melts were then allowed to be homogenized under stirring at 1200°C and poured in that preheated mould. All the alloys were analyzed by spectrochemical method and the chemical compositions of the alloys are given in Table 1. Machining of the cast samples was carried with a shaper machine to remove the uneven layer from the surface and 3×20×20 mm^3 size obtained from the samples for microhardness and electrical conductivity measurement. The alloy samples were isochronally aged at different temperatures for one hour and isothermally aged at various temperatures for different periods of time. The samples were sanded mechanically with emery papers of rough one and the one of 1500 grits. Microhardness analysis of the aged samples was performed using a Micro Vickers Hardness Tester. The knoop indenter was applied with 1Kg load for 10 seconds. An average of seven readings obtained from different locations from each sample. Electrical conductivity of the alloy in different heat treatment condition was carried out with an Electric Conductivity Meter Type 979. Thermal conductivity was calculated from those electrical conductivity data through the Wiedemann–Franz law [12]. Moreover, powder of the experimental alloys was prepared for measuring the absorbance by using UV Visible Spectrophotometer device.

The microstructural observations were executed using inverted metallurgical optical microscope. In case of using metallographic copper etchant a conventionally recommended one of Ammonium Hydroxide + Hydrogen peroxide (3%) was used where the compounds were taken in 1:1 ratio. The washed and dried samples were observed carefully in optical microscope at different magnifications and some selected photomicrographs were taken.

Table-1: Chemical composition of the experimental alloys (wt %)

Alloy	Al	Zn	Pb	Sn	Fe	Ni	Mn	Si	Cr	Sb	Cu
Cu	0.001	0.000	0.010	0.004	0.033	0.001	0.000	0.000	0.001	0.000	Bal
Cu-10Al	9.601	0.023	0.013	0.009	0.078	0.007	0.009	0.004	0.007	0.079	Bal
Cu-10Zn	0.013	10.300	0.012	0.007	0.057	0.005	0.009	0.004	0.007	0.005	Bal

3. RESULTS AND DISCUSSION

3.1 Isochronal Ageing

The variation of microhardness of Cu, Cu-10Al and Cu-10Zn alloys isochronally aged at different temperature for one hour are shown in Fig -1. It is seen that Al bearing alloy has shown marginally ageing response. Pure Cu and Zn bearing alloy have however shown a continuous softening at increasing ageing temperatures, with a steeper hardness drop beyond 250ºC. The present experimental results obviously point out that the age hardening result shown by the alloy is due to addition of Al. During solidification and ageing, various intermetallic phases are formed by reaction of Al and Cu, such as: $CuAl_2$, AlCu, Cu_4Al_3,

Cu_3Al_2, Al_4Cu_9 [13]. The main intermetallic phases which affect the hardness of the alloy are Al_4Cu_9 and Cu_3Al_2. Therefore, the increase in the hardness values of Cu-10Zn alloy is mannerism to solute hardening by the zinc solute atoms. At intermediate stage of ageing Al and Zn added alloys show a modest decrease of the hardness for the reason that dissolve of GP zones before formation of metastable phase into the alloys [14, 15].

The small variation of thermal conductivity of the experimental alloys is observed with ageing temperature (Fig -2). Initial increase of conductivity during ageing of the experimental alloys is due to stress relieving into the alloys. The subsequent drop in conductivity occurs because of the formation of fine precipitates [16].

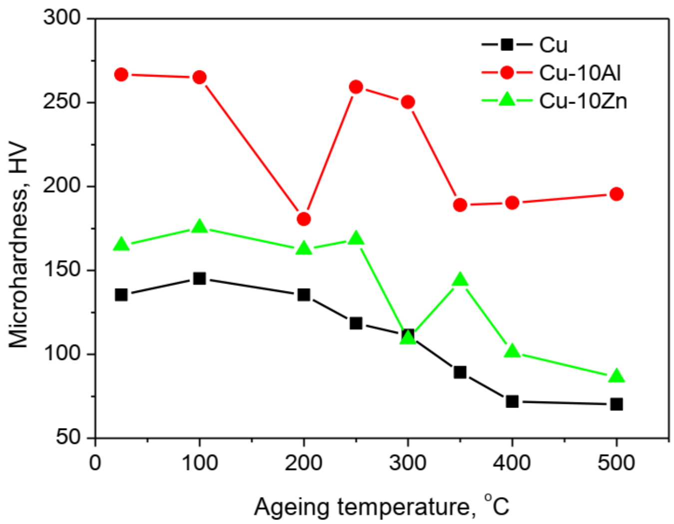

Fig -1: Variation of microhardness with temperature of the cast alloys isochronally aged for 1 hour

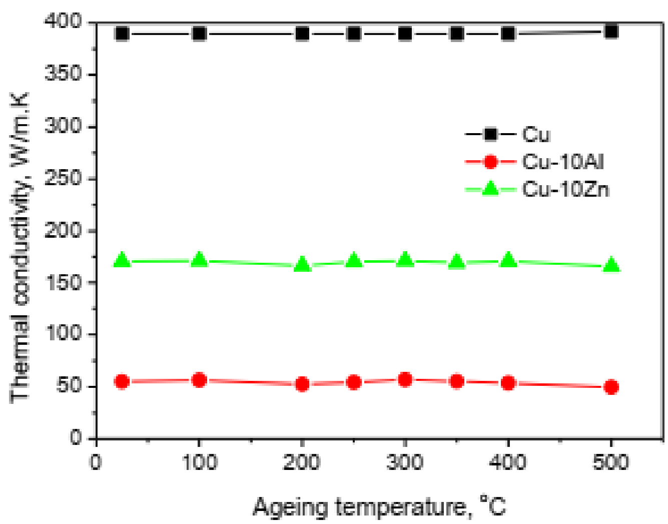

Fig -2: Variation of thermal conductivity due to isochronally ageing of the cast alloys for 1 hour

3.2 Isothermal Ageing

The hardness results of the isothermally aged alloys at different temperatures follow the more or less similar fashion of isochronal ageing. Fig -3 shows the time dependence of age hardening at a temperature of 250ºC, which is below the peak hardening temperature of the alloys as derived from the isochronal ageing. It appears from the figure that, Cu and Cu-10Zn alloy do not respond to ageing treatment. Cu-10Al alloy shows some age hardening beyond an ageing time of 60 minutes. After achievement of peak aged condition, Cu-10Al alloy has shown a softening trend followed by more or less constant value of hardness. When the ageing temperature arrives at 300ºC (Fig -4), the ageing response of the alloys is found to be quite significant, which is the peak isochronal ageing temperature of the alloys. This ageing condition is typically attained within 15 minutes. In case of Cu-10Zn alloy the hardness decreases sharply. It is because of the alloys reaches recrystallized state [17]. For isothermal ageing at 350ºC, the ageing responses are not found to be distinct since within a very short time, the hardness rises to high value for Cu-10Al alloy. Cu and Cu-10Zn alloys do not record any increasing of hardness change (Fig -5). In every cases of isothermal ageing it can be found that Cu-10Al alloy attains a drop in harnesses during ageing. In the course of ageing procedure, GP zones and metastable phases can successfully strengthen the Cu-10Al alloy and direct to the aging peak. In the period of transition from GP zones to metastable phases, it can be assumed that GP zones dissolution should be accountable for the softening of the alloy. In case of Cu-10Zn alloy further diffusional transformation has taken place on ageing at 300ºC leading to some grain coarsening of α-grains and which are still distributing inside the grains that is the cause of hardness drop at that temperature of isothermal ageing. New grain formation causes the increases of hardness of Cu-10Zn alloy at 350ºC ageing temperature.; Above 35 wt.% Zn content, the intermetallic β-CuZn (CsCl type) would be formed, which induces precipitation strengthening, so Cu-10Zn alloys usually exhibit a single α-phase FCC state which does not show remarkable age hardening effects [18]. The thermal conductivity values of the alloys aged isothermally at 300ºC go after the similar nature of isochronal ageing (Fig -6). The conductivity of the base alloy remains reasonably unchanged over the whole period of ageing. Cu-10Al and Cu-10Zn alloys show the increasing trend due to stress relieving and precipitate coarsening effects.

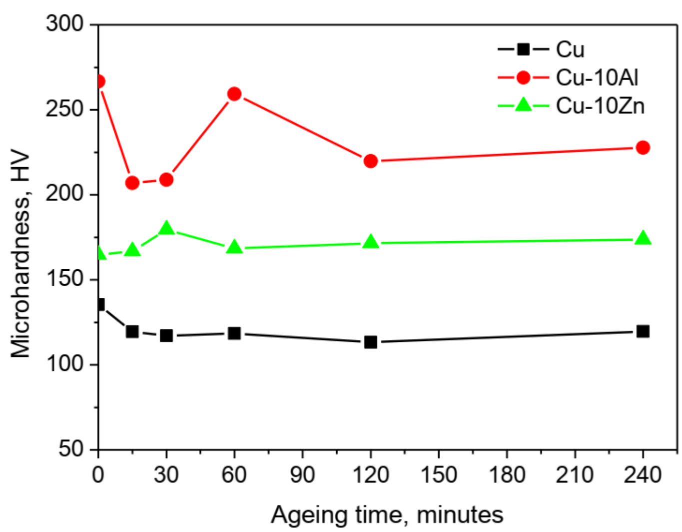

Fig -3: Microhardness evolution of the cast alloys with ageing time at 250ºC.

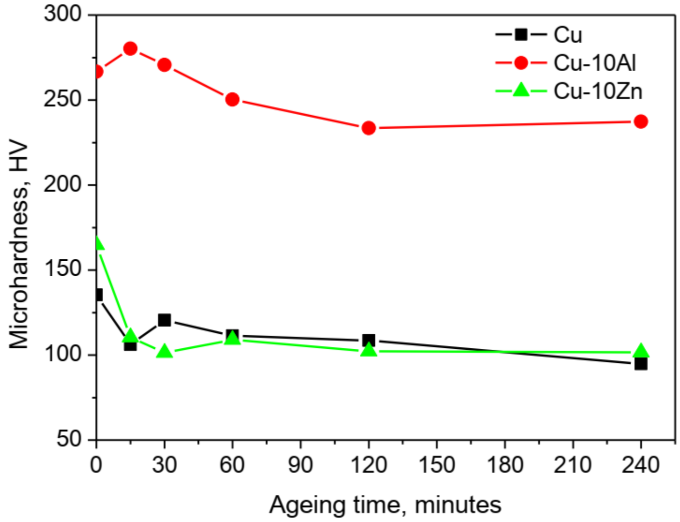

Fig -4: Microhardness evolution of the cast alloys with ageing time at 300ºC.

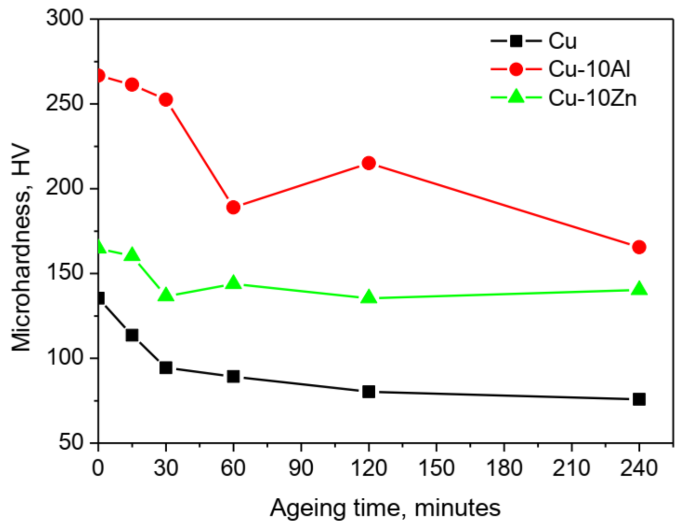

Fig -5: Microhardness evolution of the cast alloys with ageing time at 350ºC.

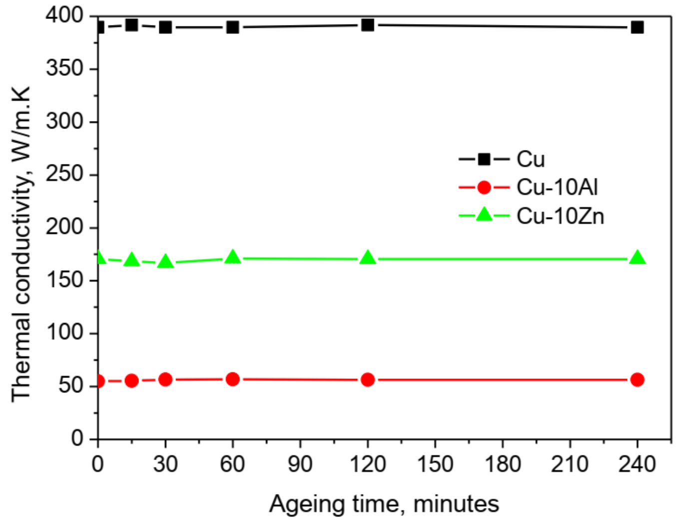

Fig -6: Variation of thermal conductivity of the cast alloys with ageing time at 300ºC.

3.3 Absorbance properties

The absorption spectrum of Cu, Cu-10Al and Cu-10Zn alloys, as a function of the wavelength of the incident light is shown in Fig -7. The absorption spectrum shows the wavelength is lower for Zn added alloy and Al added alloy shows marginally higher absorption at low wavelength. Because different materials are capable to absorb different wavelengths, the dominance of transmittance varies with the wavelength even for the same concentration of Cu. Coarse grain of Cu-10Al alloy causes the variation of absorbance by means of pure copper. Earlier it was establish that the transition increases to some extent in energy with Zn concentration. These transitional energies are identical for the alloy in the entire α-phase region. This variation is obvious, because the absorption is the opposite phenomena of transmittance. The α-brass phase occurs when the Zn content is below about 35 wt.% and it has a disordered, substitutional face centered cubic (FCC) structure. As the Zn content increases the color transforms from the reddish hue of pure Cu to the bright yellow of brass. Associated with this color change, the optical absorption edges shift upwards in energy since the Zn content increases [19, 20].

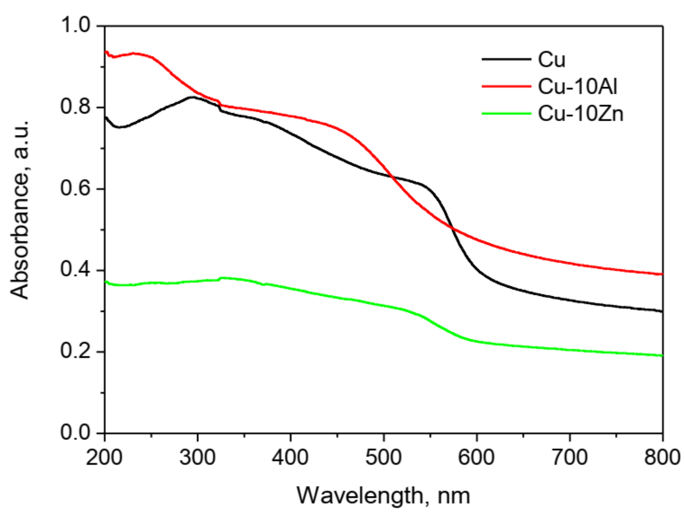

Fig -7: The absorbance as function of wavelength for Cu, Cu-10Al and Cu-10Zn alloys

3.4. Optical microscopic observation

The optical microstructure of Cu, Cu-10Al and Cu-10Zn alloys at cast state is shown in Fig -8. The microstructure of cast copper is fashioned by non-uniform grains with very dissimilar sizes. The surface cracking, porosity, and the formation of internal cavities of the metal are high because of the copper's reactivity [21]. The microstructure of Cu-10Al is found to consist of three phases namely α-phase, retained β' phase and numerous K-phases (κi , κii, κiii, κiv) [22]. K-phases are divided into four main types: κI, κII, κIII and κIV. The microstructure of Cu-10Zn alloy reveals the presence of a single solid phase which consists of a solid solution of zinc in alpha copper. This is predictable that zinc has complete solid solubility in copper up to 35% supported on the Cu-Zn phase diagram; [23].

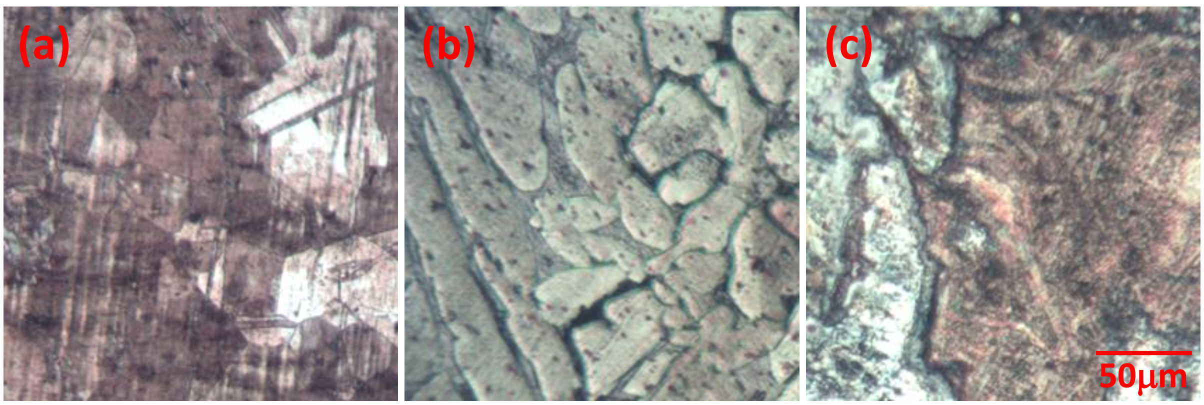

Fig -8: Optical micrograph of cast alloys a) Cu, b) Cu-10Al and c) Cu-10Zn

Fig -9 shows the optical micrographs of the experimental alloys after ageing treatment at 400°C for one hour. Some annealed twins can be found in the annealed pure copper grains due to recrystallization property and most of the annealed twins traverse through the grain completely. (Fig -9. a) [24]. The microstructure of Cu-10Al aged alloy contains large numbers of κ precipitates (Fig. 9. b). The portion of the α- phase increases. The spaces between polyhedral grains begin to be similar to an irregular network. The grains surround by annealing twins and spherical particles of κ precipitate. Dendritic structure with a few precipitates may be visible. It can be seen from Fig –

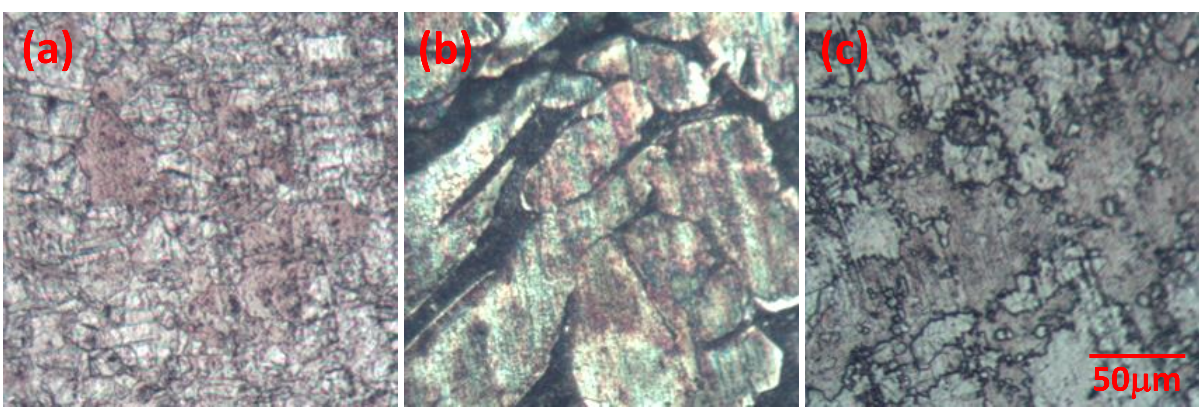

Fig -9: Optical micrograph of cast alloys aged at 400ºC for 1 hour, a) Cu, b) Cu-10Al and c) Cu-10Zn

Fig -9. c that the grain size of aged Cu-10Zn alloy is higher than the original pure copper because of grain growth under high temperature. Grains with a few twins and precipitates on boundaries are observed for aged alloy. The microstructure is a mixture of recrystallized grains and coarse nonrecrystallized grains. A homogenized recrystallized microstructure is observed in Cu-10Zn alloy as well as in pure copper

3.5. Quantitative analysis

Table 2 describes the changes observed through the investigation in the properties due to addition of 10wt% Al and Zn into copper. It clearly shows that, the percentage of overall gain for hardness, due to solid-solution strengthening with the expenses of thermal conductivity. An absorption property of Cu slightly increases due to addition of Al but decreases with the addition of Zn.

Table-2:. Overall chance (%) in properties due to addition of Al and Zn by 10wt% into Cu

Properties	Cu	Cu-10Al	Cu-10Zn
Hardness (HV)	135.4	266.7 (+96.8%)	164.7 (+21.6%)
Thermal conductivity (W/m.K)	389.5	55.10 (-85.6%)	170.6 (-56.2%)
Absorption (a.u)	0.635	0.654 (+3.0%)	0.313 (-50.7%)

4. CONCLUSIONS

Pure Cu, Cu-10Al and Cu-10Zn copper-based alloys obtained by casting flowed by different heat treatment. According to the experimental results it is obvious that the addition of Al into Cu increases the hardness by 96.8% followed by Zn addition by 21.6% due to solid-solution hardening. Additionally Al form hard and brittle intermetallic during ageing which improves the hardness of the alloy. Addition of Al and Zn into copper results the decreases of thermal conductivity by 85.6% and 56.2% respectively. In terms of absorption, Zn plays the greater role as compared to Al. As cast microstructure shows different phases of grains but aging at 400°C for one hour all the alloys reach partially re-crystallized state.

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