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Phase Transformations in the System Cu-Zn-Al under Conditions Far from Equilibrium

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Abstract. It is shown that the alloy Cu-Zn-Al is a multiphase material. Under equilibrium conditions this alloy can form an α-phase (FCC crystalline lattice) and a β-phase (simple cubic crystalline lattice) based on copper. The possibility of formation of a γ-phase due to a three-component alloy composition is revealed. It is established that different chemical composition of the copper-based solid solution (alloys with zinc or alloys with aluminum), different concentration of the second element in a solid solution leads to the fact that within the same type of the crystalline lattice there is a certain amount of α- and β-phases, differing in the parameter value of the crystalline lattice. The possibility of formation of powder alloys with an x-ray amorphous and a nanocrystalline structure using the plasma chemical synthesis methods is demonstrated. A wide variety of binary phases, each with different concentrations of zinc and aluminum in a solid copper-based solution is revealed. These results indicate that plasma-chemical synthesis of metal alloy powders is accompanied by separation of elements. Powders of the ternary composition are not detected.

INTRODUCTION

Conventional methods for production of fine metal powders, such as electric explosion of conductors, mechanical grinding in mills, spraying in melts [1], evaporation-condensation [2], reduction of oxide with hydrogen, hydrogen-containing gases, carbon or carbon monoxide, autoclave and electrolytic recovery from solutions [3, 4] are widespread. However, such methods have several disadvantages, the main are: the use of metal oxides as the initial powder, relatively low depressiveness of particles, and the use of explosion-flammable gases (hydrogen, carbon monoxide etc.) as reducing agents. In this respect, plasma-chemical methods for production of metal powders by denitration from nitric acid solutions containing reducing agents have a number of significant advantages:

– exclusion of large amounts of fire-hazardous gases from the technology (substances that are fire-explosion-proof under normal conditions can be used as a reducing agents);

– possibility of recycling wastes from metal production which are in the form of solutions, bypassing the deposition stage and production of their oxides;

– high depressiveness of powders;

– possibility to produce ultrafine-dispersed powders of alloys with many metals (such as copper, iron, cobalt) with unique properties, such as high ductility combined with corrosion resistance, valuable electrical and magnetic properties.

The plasma-chemical method for production of nanostructured simple and mixed powders of oxides, metals, and alloys from pre-prepared solutions of a given composition with the use of high-frequency low-temperature plasma is highly productive, low-stage, does not require reagents for precipitation of salts, does not include process steps for filtration and calcination of precipitations, and the produced powders are chemically active.

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The aim of the work is the analysis of the structure and phase composition of powders of the alloy Cu−Zn−Al produced using the HF-plasma-chemical denitration methods.

FEATURES OF STRUCTURAL-PHASE STATES IN SYSTEMS Cu−Zn, Al-Cu, Al-Zn and Al-Cu-Zn

We shall briefly give a set of phases that are found on equilibrium binary diagrams in systems Al-Cu, Al-Zn, Cu−Zn according to the handbook [5].

System A1−Zn. In this system, the existence of two nonvariant equilibria (eutectic L↔β+(Al)+β and monotectoid α_1↔α+ β has been revealed, where α1 and α are solid solutions based on Al and β based on Zn) (Fig. 1).

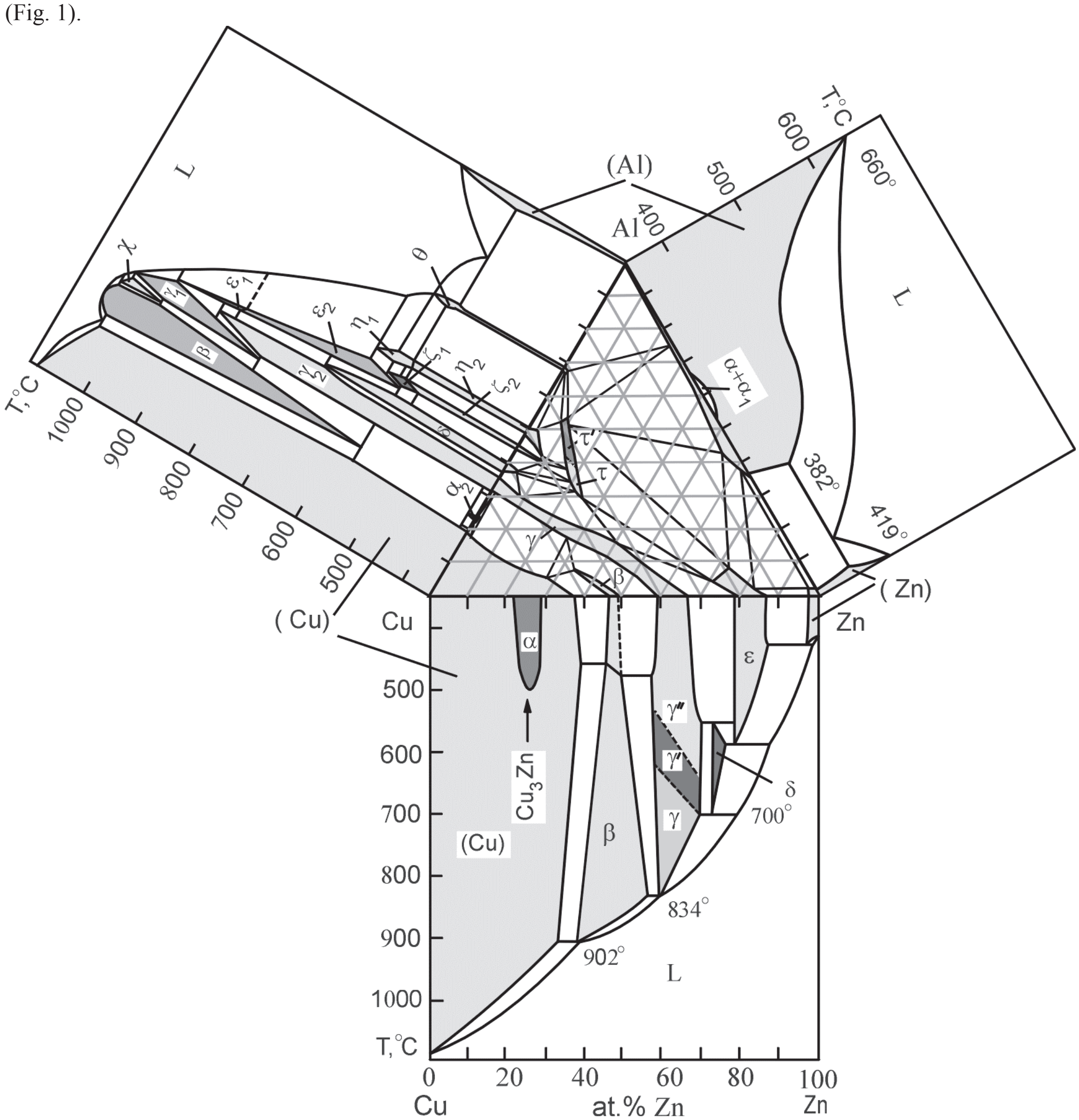

FIGURE 1. Binary diagrams of systems Al-Cu, Al-Zn, Cu-Zn and an isothermal section of the ternary system Al-Cu-Zn at 350°C [7]

System A1−Cu. In the system Al-Cu a very large number of phases of the order 15 have been revealed. Two phases (Cu) and (A1) are solid solutions based on Cu and A1, respectively. Six phases are formed with the participation of a liquid phase: β (space group $Im\overline{3}m$), χ (sp.gr. is not defined), γ_1 ($I\overline{4}3m$), ε_1 ($Pm\overline{3}m$), η_1 (*Pban*) and θ (solid solution based on the compound $CuA1_2$, sp. gr. *I*4/*mcm*). The remaining 7 phases are formed as a result of transformations in the solid state: γ_2 (solid solution based on the compound Cu_9Al_4, sp. gr. $P\bar{4}3m$), α_2(*I4/mmm*), ε_2 (*P*6_3*/mmc*), δ (*R*3*m*), ζ_1(*P*6*/mmm*), ζ_2(*Imm*2), η_2(*C*2*/m*) (Fig. 1).

System Cu–Zn (Fig. 1). In the system Cu–Zn the existence of six phases has been revealed: solid solution based on Cu is formed by crystallization from a liquid phase, in which as a result of the phase transformation it gives two ordered phases α_1(hR9) and α_2. Phases β($Im\bar{3}m$), γ($I\bar{4}3m$), δ($P\bar{6}$), ε (*P*6_3*/mmc*) and the solid solution based on (Zn) are formed by peritectic reactions. The phase β'($Im\bar{3}m$) is formed from the β phase. The phase γ exists in four modifications: γ''', γ'', γ' in different temperature ranges.

System Al–Cu–Zn (Fig. 1). On isothermal sections of the ternary system Al-Cu-Zn there are extended homogeneity regions of intermetallic compounds β, γ, ε and a disordered solid solution based on the α-phase. Figure 2 shows isothermal sections of the ternary system Al-Cu-Zn at different temperatures. These isothermal sections show that homogeneity regions of phases β, ε, τ and τ' significantly increase in the size with an increase in the temperature. This indicates an increase in the stability of these phases. The homogeneity region of the γ-phase changes its shape with an increase in the temperature. It should be noted that at the temperature of 500 °C the δ-phase is detected, which at the temperature of 550 °C begins to occupy a significant area on the isothermal section.

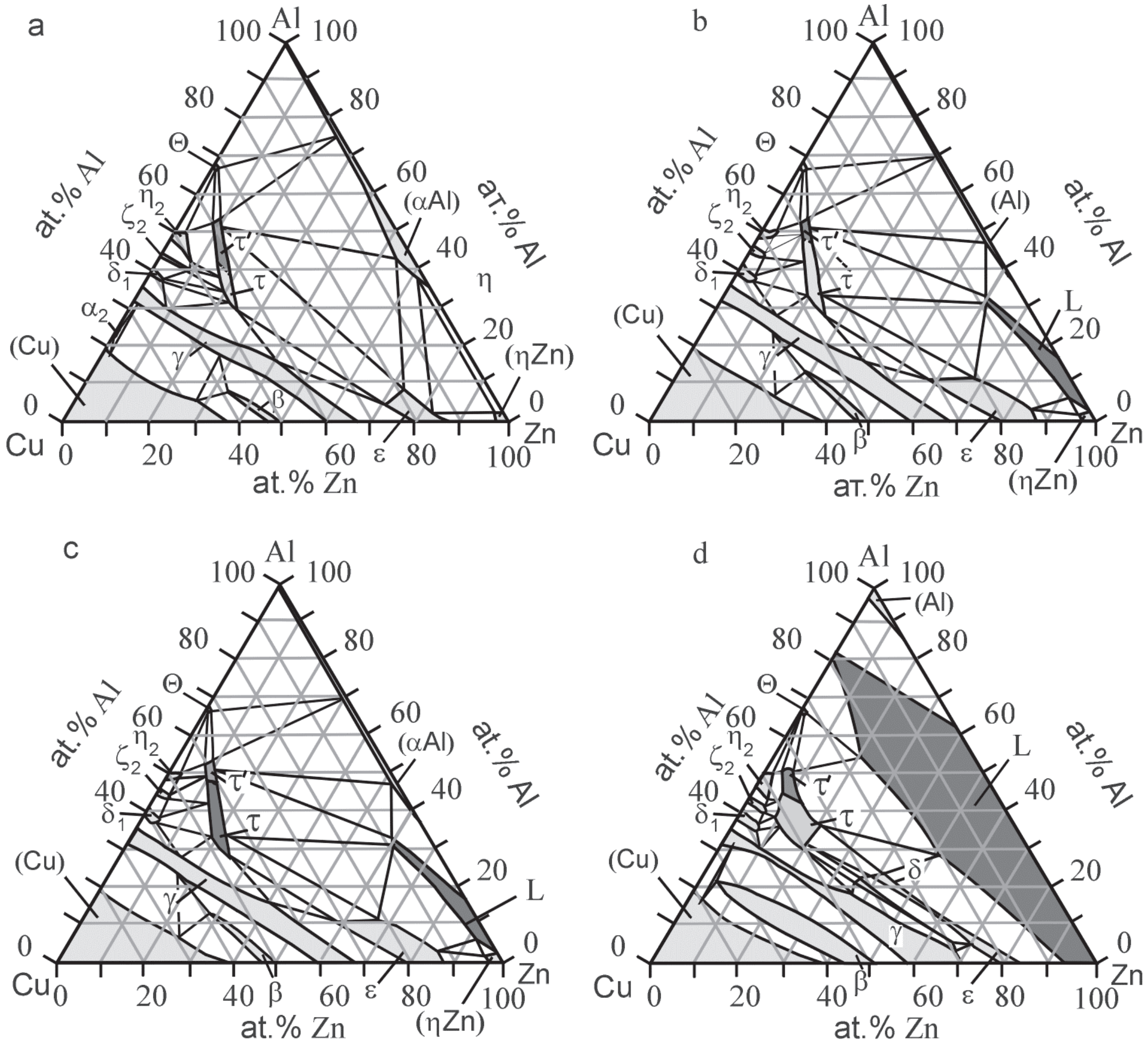

FIGURE 2. Isothermal sections of the ternary system Al-Cu-Zn at different temperatures: a – 350 °C; b – 400 °C; c – 450 °C; d – 550 °C; [10-13]

The ternary phase τ exists in the range of the composition $Al_{34}Cu_{40}Zn_{20}$ and at temperatures below 740 °C. The phase τ has an ordered lattice based on the B2 phase (Table 1). A feature of this phase is that at low temperatures the range of its existence is divided into two (Fig. 1 and Fig. 2). One range has the τ phase. The other range has the τ' phase with a rhombohedral structure (Table 1). In [3] it has been found that the τ' phase has a high concentration of structural vacancies, which leads to lattice distortion of the τ phase with the B2 structure to the rhombohedral.

The discovered in the system ternary compound $Cu_{10}Al_6Zn$(T) exists in two modifications. The compound T with a BCC-lattice exist in alloys with a content of Al up to 20% (by weight) Al, in alloys with higher aluminum content there is a modification T' with a pseudocubic lattice [6,7].

Table 1. Structural data of phases in the system Al-Cu-Zn

Composition, temperature range	Pearson symbols	Prototype	Elementary cell parameters, nm	Source
τ, ≈$Cu_5Zn_2Al_3$ < 740 °C	≈*cP*2	CsCl	*a*=0.2904	[11]
$Cu_{46}Zn_{20}Al_{34}$			*a*=0.2932	[11]
τ ′, $Al_{34}Cu_{40}Zn_{20}$ < 740 °C	rhombohedral		*a*=5.8694±0.0020, α=27.35°±0.18	[13,14]

Thus, the above mentioned data show that copper-based α– and β–phases can be formed under equilibrium conditions in the alloy Cu – 20.9 at. % Zn – 11.5 at. % Al (the existence of the γ-phase is also possible as a result of a three-component composition of the alloy). The α-phase has a FCC-lattice, the β-phase has a simple cubic lattice [5-9]. These phases are distinguished within one type of a crystalline lattice by parameter values of the lattice. This is due to different chemical compositions of the copper-based solid solution (alloys with zinc or alloys with aluminum) and different concentrations of the second element in the solid solution. It shall be noted that the ternary phase is not formed in the investigated alloy under equilibrium conditions.

RESULTS AND DISCUSSION

Powders of the alloy Al-Cu-Zn were produced using the plasma-chemical method [15]. Morphological study of the powder was performed using diffraction electron microscopy methods [16, 17]. Formation of powders of several space forms has been revealed as a result of the performed studies. The particles of the quasi-spherical form are most common (Fig. 3). Particle sizes range from 10 nm to 150 nm, the average particle size is 46.5 nm.

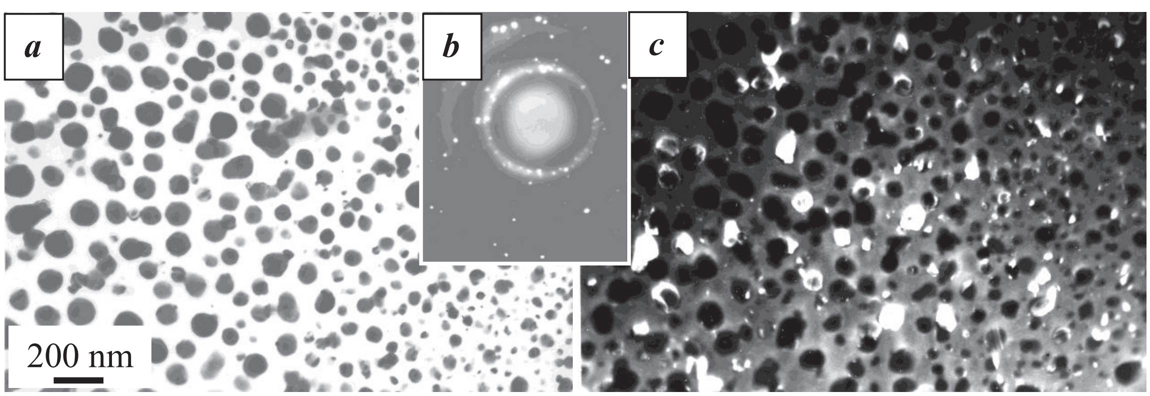

FIGURE 3. The electron microscope image of powder particles of the alloy Cu-Zn-Al; a – light field; b – micro-electron diffraction pattern; c – dark field, obtained in reflexes of the first diffraction ring

Another morphological type of the investigated powder is polycrystalline films, which crystallites are spherical with an average size of 12 nm (Fig. 4).

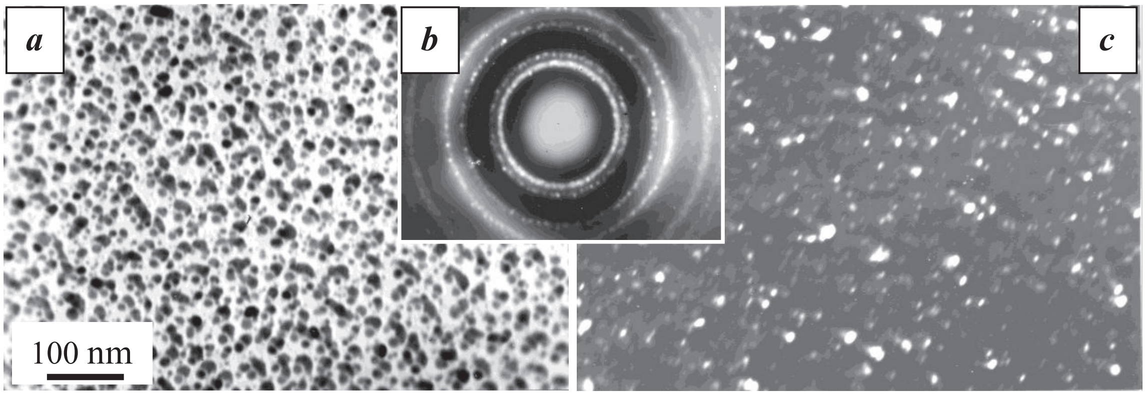

FIGURE 4. The electron microscope image of powder particles of the alloy Cu-Zn-Al; a – light field; b – micro-electron diffraction pattern; c – dark field, obtained in reflexes of the first diffraction ring

Films, as a rule, interact with another morphological type of powder – splinter-shaped particles. Very rarely splinter-shaped particles are located separately from polycrystalline films (Fig. 5). The dark field image (Fig. 5) shows that splinter-shaped particles are single crystals. Sometimes, these particles have a facetted shape. The size of splinter-shaped particles is very diverse and varies from 30 nm to 270 nm.

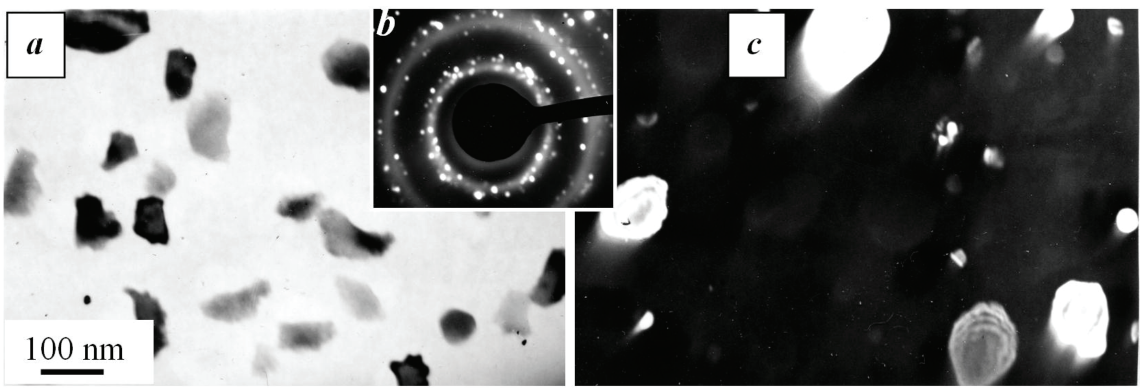

FIGURE 5. The electron microscopic image of powder particles of the alloy Cu-Zn-Al; a – light field; b – micro-electron diffraction pattern; c – dark field, obtained in reflexes of the first diffraction ring

The phase analysis of the powder was performed by indexing of micro-electron diffraction patterns [16-18]. It has been established that micro-electron diffraction patterns have a ring structure (Fig. 3 – Fig. 5). From the ratio of the radii of diffraction rings it follows that data of the micro-electron diffraction pattern are formed mainly by the phase with a FCC-lattice. In some cases, there are rings belonging to a simple cubic lattice. In the studied micro-electron diffraction patterns there are no rings that belong to the BCC-lattice. Ring micro-electron diffraction patterns obtained from the films have a complex structure. Each diffraction ring (there are up to eight rings) consists of a discretely located reflexes with different diffraction radii R_{hkl}. This suggests the existence of a phase with a variable parameter of the crystalline lattice, which may be due to the heterogeneity of the chemical composition of the powder or, what we think is preferable, due to the presence of a set of phases allowed by equilibrium diagrams.

The analysis of micro-electron diffraction patterns obtained from the investigated powder allowed determining values of the radius-vector R_{hkl} of diffraction rings. The obtained values were compared with the values of radius-vectors (interplanar spacings) calculated for diagram phases observed in alloys Cu-Zn and Cu-Al, and having the FCC and simple cubic lattices. The comparison of the calculated and the experimentally obtained values of radius-vectors showed that each diffraction ring (in the FCC installation this rings are of the type {111}, {002}, {022}, {113}, {133}, etc.) includes reflexes of all diagram phases (Fig. 1), as parameters of crystalline lattice of these phases are close to each other. The β-phase gives several individual diffraction rings, which do not coincide with rings of the α-phase. This enables to virtually unambiguously identify the β-phase during indexing of micro-electron diffraction patterns. Thus, from the analysis of the obtained results it follows that in the general case microdiffraction rings can have a very complicated structure – each diffraction ring may contain reflexes of a certain set (up to eight) of different radius-vectors. These facts indicate that the powder of the alloy Cu-Zn-Al produced using plasma-chemical synthesis methods is a multiphase material and may contain almost all phases identified in the formation of the given alloy in equilibrium conditions.

CONCLUSION

The analysis of phase diagrams has shown that under equilibrium conditions in the alloy Cu-Zn-Al two-component (α-phases, FCC-crystal lattice, and β-phases, simple cubic crystalline lattice) and three-component (γ-phase) copper-based phases can be formed. Different chemical composition of the copper-based solid solution (zinc alloys or aluminum alloys) and different concentration of the second element in the solid solution leads to the fact that within the same type of the crystal lattice there is a certain amount of α- and β-phases, differing in the parameter value of the crystalline lattice. The possibility of formation of powders of the alloy Cu-Zn-Al with an X-ray amorphous and nanocrystalline structure using plasma-chemical synthesis methods has been shown. A wide variety of binary phases, each with different concentrations of zinc and aluminum in the copper-based solid solution has been revealed using micro diffraction electron microscopy analysis methods. These results indicate that plasma-chemical synthesis of metal alloy powders is accompanied by separation of elements. Formation of a powder with a three-element composition has not been revealed.

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