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Electrical resistivity of liquid lead-free solder Sn-0.7Cu-xBi alloys

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Abstract

Liquid structure plays significant role in solid microstructure and mechanical properties during material processing. In this paper, the temperature dependence of electrical resistivities in liquid Sn-0.7Cu-xBi alloys has been investigated with DC four-probe method. The results show that anomalous changes can be observed on resistivity-temperature curves at certain temperatures in two experimental cycles, which indicate the existence of liquid structural transitions in the melts at elevated temperature, and the transitions are reversible after first cycle heating. The content of Bi has a noticeable influence on the turning temperature and resistivity-temperature curve shape. The anomalous behaviour of the electrical resistivity--temperature curve is analysed from the viewpoint of short-range order. These results will help to enrich the phenomenology of liquid field, and provide some scientific reference to the innovation of lead-free solder manufacturing.

K e y w o r d s: lead-free solder, electrical resistivity, liquid structural transition, Sn-Cu-Bi alloys

1. Introduction

It is acceptable that melt structure has direct effects on the microstructure and properties of as-cast materials. Many scholars have optimised the microstructures of castings using particular techniques such as melt thermal treatment and melt overheating [1–6]. However, the inherent relationship between the solid structure and the anomalous change of melt physical properties has not been thoroughly understood. It is noteworthy that growing attention has been given to liquid-liquid structure transition in the field of condensed matter physics, material processing and metallurgy in recent years. For example, temperature--induced liquid-liquid structure transitions (TI-LLSTs) have been observed and confirmed in one-component systems and their alloys at the temperature far above their liquidus by the electrical resistivity method [7–9], X-ray diffraction [10, 11], revised internal friction method [12, 13], and viscosity [14, 15]. It is essential to carry on extensive and in-depth investigation on TI-LLSTs and their potential use in different melts.

Traditional Sn-Pb solders have been commonly used in electronic packaging interconnects due to their excellent properties and low cost. However, developing alternative lead-free solders has become an inevitable trend by the consensus of lead's hazards to human. At present, the main Sn-base lead-free solders, which have been developed, are Sn-Ag, Sn-Cu, Sn-Ag-Cu, Sn-Zn, Sn-Bi alloys etc. Among the lead-free solders, the eutectic Sn-Ag-Cu and Sn-Cu alloys have been recognized as the most promising candidates to replace traditional Sn-Pb solders [16–20]. So far, the studies on lead-free solders materials mainly focus upon the selection of components, optimisation of the mixture ratio of components, and influence of minor elements (such as rare earth elements) on various properties of lead-free solders. The addition of a certain amount of Bi, one of the popular alloying elements to lead-free solders, can reduce the melting temperature and increase mechanical properties of the solders [21–24]. Although a great number of researches on improving the solders' performances by adding minor elements have been carried out, the joint reliability and processing properties of lead-free solders are still inferior to those of the traditional Sn-Pb solders. Moreover, manufacturing processes of lead-free solders have rarely been investigated up to now. In this paper, temperature de-

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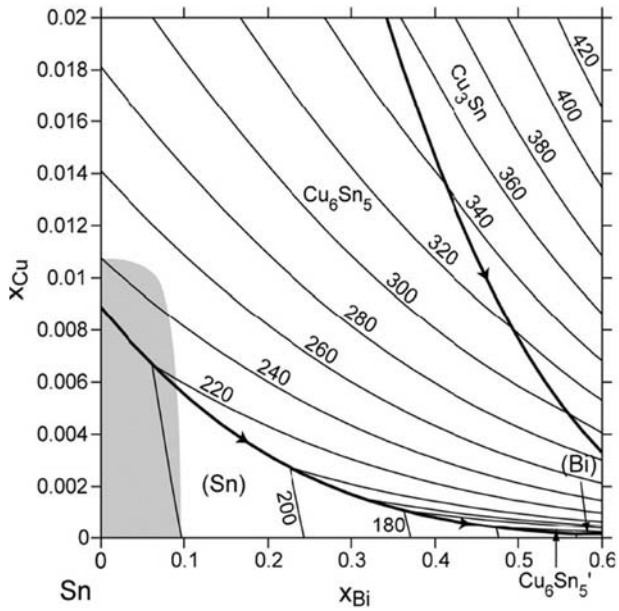

Fig. 1. A part of phase diagram for the Sn-Cu-Bi system.

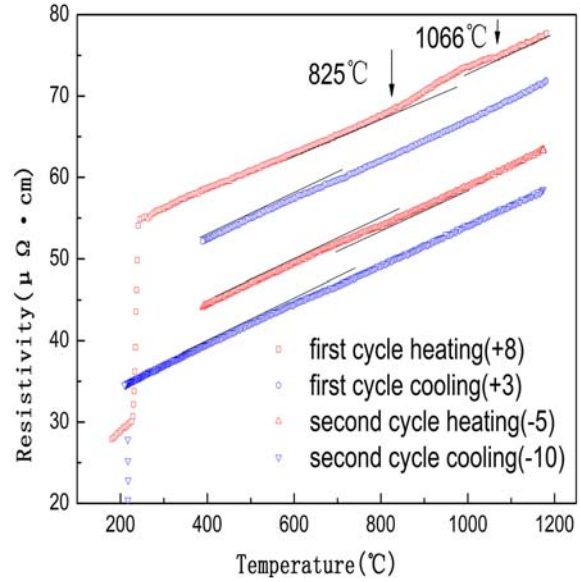

Fig. 2. Electrical resistivity-temperature curves of Sn-0.7Cu alloy in two heating and cooling cycles.

pendence of liquid transitions has been studied, which can provide new phenomenological basis for better understanding the liquid structure and the fundamentals to optimise and innovate manufacturing processes of lead-free solders.

The temperature dependence of electrical resistivities of liquid Sn-0.7Cu-xBi (weight percent) lead-free alloys with different Bi components was surveyed by electrical resistivity experiments. The results show that there are anomalous changes in some temperature ranges on the resistivity-temperature (ρ-T) curves, which indicate the existence of liquid structural transition in Sn-0.7Cu-xBi melt above liquidus. Moreover, the turning temperature and the curve shape of the anomalous transitions vary with different contents of Bi in Sn-Cu-Bi ternary melts.

2. Experimental procedure

Sn-Cu-Bi phase diagram is shown in Fig. 1 [25], and the shaded area represents the composition scope with suitable freezing ranges (< 35 ℃) for candidate solder alloys. According to the shaded area, five types of Sn-0.7Cu alloys containing 0, 3, 5, 7.5, and 10 wt.% Bi were chosen for the ρ-T experiments. All of the Sn-Cu-Bi samples were prepared with Sn, Cu, and Bi granules of high purity (4N). The melts were heated to 400 ℃, held for 1 h covered with KCl-LiCl melts, and then poured into quartz cells for the following experiments. During the entire melting process, the samples were shaken mechanically three times for component homogenisation. The thermal expansion of the quartz was so small that the size variation with temperature could be neglected.

The electrical resistivities were measured with the DC four-probe method, and the quartz cell was placed in the homogeneous heat area of the furnace to eliminate thermal electromotive force (EMF) as much as possible. Furthermore, the DC current-reversal technique was used to cancel the thermal EMFs that might be caused by the connection points and temperature fluctuations in the test leads. The potential drop was measured with KEITHLEY-2182 nanovoltmeter with the PF66M current source providing the constant current. Tungsten wires with diameters of 1 mm were employed as current and potential electrodes. The whole measuring process was under the protection of pure argon (5N). The resistivities were measured continuously during two heating and cooling cycles at the constant rate of 5 ℃ min^{-1} in order to probe the reversibility of TI-LLSTs. In addition, the ρ-T patterns of pure tin and bismuth were quoted for comparison with those of Sn-Cu-Bi alloys.

3. Results and discussion

The values of electrical resistivity of Sn-0.7Cu-xBi (x = 0, 3, 5, 7.5, and 10) alloys versus temperature are shown in Fig. 2 to Fig. 6. Obvious slope changes can be observed on the ρ-T curves of Sn-0.7Cu and Sn-0.7Cu-10Bi melts in the first cycle heating, and evident hump phenomenon on the ρ-T curves of Sn--0.7Cu-5Bi and Sn-0.7Cu-7.5Bi melts. Two anomalous changes can be observed on the ρ-T curve of Sn-0.7Cu--3Bi in the first heating process: one occurs in a low-

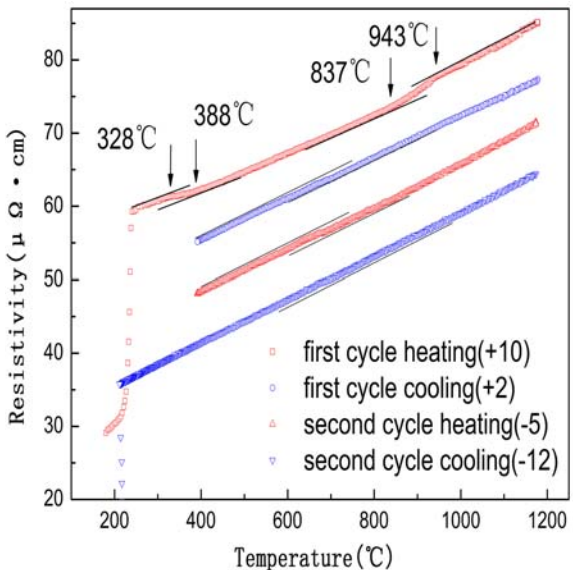

Fig. 3. Electrical resistivity-temperature curves of Sn-0.7Cu-3Bi alloy in two heating and cooling cycles.

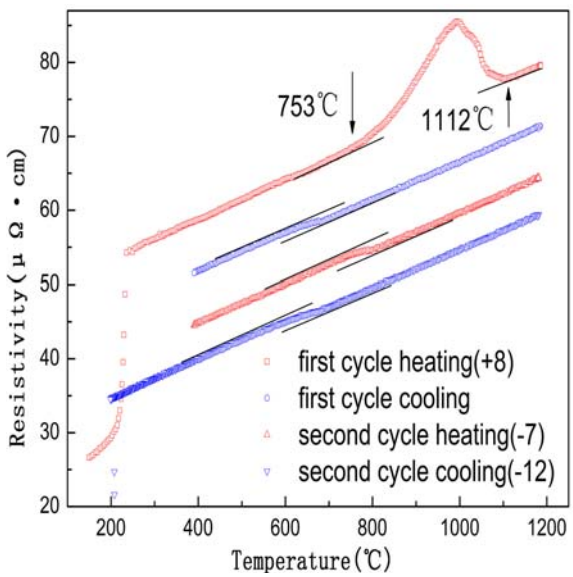

Fig. 4. Electrical resistivity-temperature curves of Sn-0.7Cu-5Bi alloy in two heating and cooling cycles.

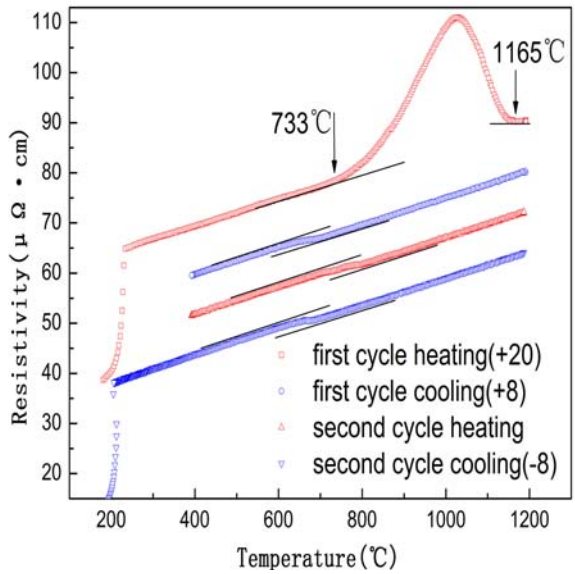

Fig. 5. Electrical resistivity-temperature curves of Sn-0.7Cu-7.5Bi alloy in two heating and cooling cycles.

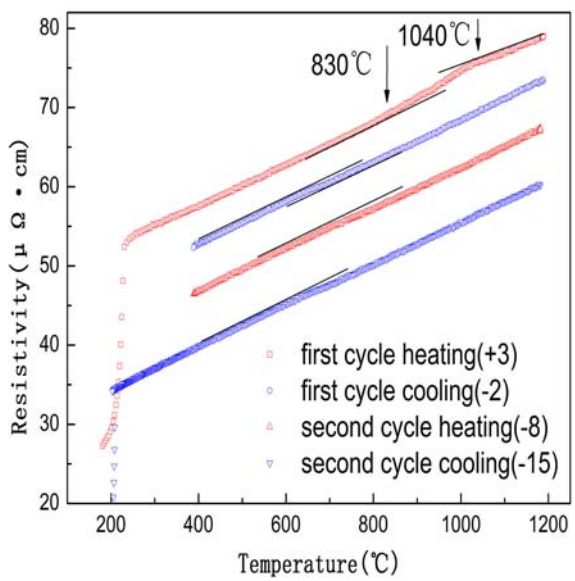

Fig. 6. Electrical resistivity-temperature curves of Sn-0.7Cu-10Bi alloy in two heating and cooling cycles.

-temperature range near the melting point, the other occurs in a high-temperature zone far above the liquidus. The turning points have been pointed out on ρ-T curves for all samples, and the anomalous changes are reversible after the first cycle heating. The anomalous changes of temperature dependence resistivity indicate that TI-LLSTs occur in liquid Sn-Cu-Bi alloys, and the possible TI-LLSTs are reversible after first cycle heating.

The ρ-T curves of pure Sn and Bi are shown in Figs. 7 and 8 [26]. There are obvious anomalous slope changes on both heating and cooling on the ρ-T curves of Sn melt in two experimental cycles, while evident hump anomalous changes are only observed on the ρ-T curve of Bi in the first heating process, which is irreversible in the subsequent cooling and heating cycles. Since electrical resistivity is one of the physical properties sensitive to structures, it is assumed that TI--LLSTs occur in liquid Sn and Bi, and the TI-LLST in liquid Sn is reversible, while irreversible in liquid Bi. Comparing the TI-LLST character of Sn-Cu-Bi melts with those of liquid Sn and Bi, the reversible char-

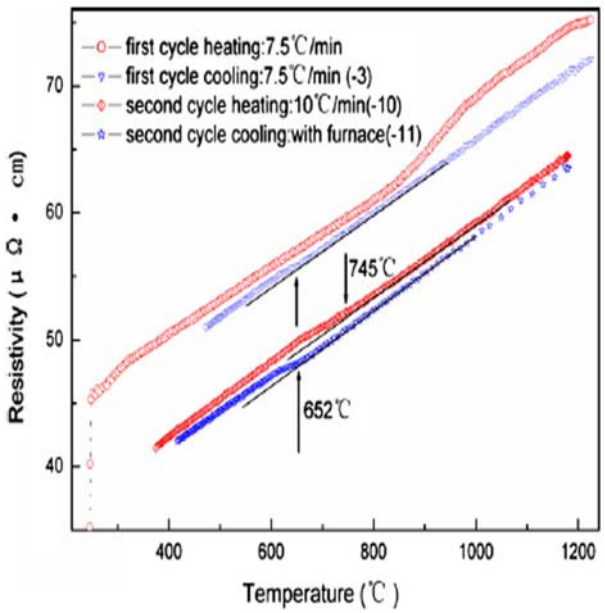

Fig. 7. Electrical resistivity-temperature curves of pure Sn in two heating and cooling cycles.

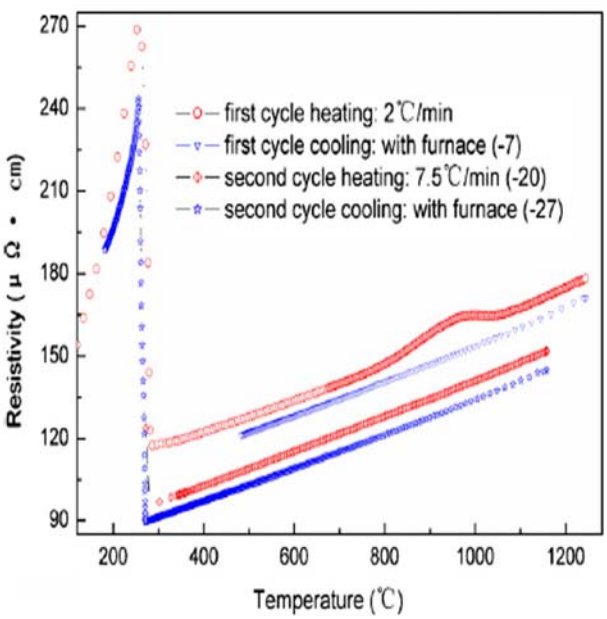

Fig. 8. Electrical resistivity-temperature curves of pure Bi in two heating and cooling cycles.

acteristics of their TI-LLSTs are very similar to that of liquid Sn, which suggests that Sn or Cu may play an important role on the reversible TI-LLSTs in Sn--Cu-Bi melts. Furthermore, in Sn-0.7Cu-5Bi and Sn--0.7Cu-7.5Bi melts, hump phenomenon resembles that of liquid Bi, and the reversibility of TI-LLSTs is more obvious than that of the others. In addition, temperature coefficient of resistivity (TCR) of Sn-Cu-Bi melts and liquid Sn, Bi in the first heating cycle is shown in Table 1. It can be seen from Table 1, that TI--LLSTs increase the TCRs of liquid Sn, Bi, Sn-0.7Cu, and Sn-0.7Cu-3Bi melts, while decrease those of Sn--0.7Cu-5Bi, Sn-0.7Cu-7.5Bi, and Sn-0.7Cu-10Bi melts. So we infer that the content of Bi in Sn-Cu-Bi alloys has a great effect on the characteristics of TI-LLSTs.

Table 1. Temperature coefficient of resistivity of Sn-Cu-Bi melts and liquid Sn, Bi in the first heating cycle

Melts	Temperature coefficient of resistivity (10^{-10} Ω m℃$^{-1}$)	
	Before liquid structural transition	After liquid structural transition
Sn-0.7Cu	2.214	2.428
Sn-0.7Cu-3Bi	2.357	2.560/3.201*
Sn-0.7Cu-5Bi	2.646	2.490
Sn-0.7Cu-7.5Bi	2.652	0.751
Sn-0.7Cu-10Bi	2.607	2.262
Liquid Sn	2.635	2.931
Liquid Bi	5.889	7.422

* 2.560 is the TCR after the first TI-LLST, 3.201 is the TCR after the second TI-LLST

Moreover, according to [27], the liquid structure of Sn-0.7Cu solder had been studied at 260, 330, 400℃ by using high temperature X-ray diffractometer. The experimental results showed that only short-range order (SRO) structures were detected in molten Sn--0.7Cu solder under the above-mentioned temperatures. Compared with the liquid structure of Sn in [28], it can be inferred that the liquid structure of Sn-0.7Cu solder is similar to that of Sn in a low-temperature range above liquidus. In addition, according to our recent research, Cu-Sb76.5 melt was also found to present similar reversible changes on ρ-T curve while pure Sb melt presented irreversible change on ρ-T curve. The above-mentioned reversible changes on ρ-T curves of Cu-Sb, Sn, and Cu-Sn-Bi can help us to infer that the reversible TI-LLSTs in Sn-Cu-Bi melts are mainly caused by Sn or Cu.

According to the nearly free electron (NFE) model [29], the electrical resistivity of liquid alloys is given by $\rho = \hbar K_\mathrm{f}/n_\mathrm{e}e^2L_0$, where $\hbar$ is the Planck constant, K_f is the Fermi wave number, e is the electron charge, n_e is the electron density, and L_0 is the mean free path of the conduction electrons. From the ρ-T curves of the samples, the resistivities increase linearly with temperature rising from the liquidus to the turning points, that is to say, based on the NFE model, $1/n_\mathrm{e}L_0$ increases linearly with temperature rising from liquidus to the turning point, and the uneven changes of their resistivities reflect the anomalous change of $1/n_\mathrm{e}L_0$ at the turning points, which can be attributed to the uneven change in n_e due to the break-

ing of previous bonds and formation of new chemical bonds, or the discontinuous change in mean free path L_0 of conduchtion electrons, or both. It is generally agreed that the atomic bonds of crystals are only partly broken on melting and lots of minor short--range ordering domains exist in the melts. It is reasonable to assume that Sn-Sn, Bi-Bi, Cu-Cu, Sn-Bi, Sn--Cu short range orders derived from the corresponding solid crystal still remain in liquids within higher temperature range, and the resistivity changes continuously and smoothly with temperature-rising. When the melts are heated to the turning points in the first heating process, the kinetic energy of the atoms becomes high enough to overcome the energy barrier, and then the previous bonds such as Sn-Sn, Bi-Bi, Cu-Cu, Sn-Bi, Sn-Cu break, meanwhile, new bonds generate; or the previous local micro-domains dissolve to make the high temperature melts more disordered. Either the old bonds break to form new SROs or the local domains dissolve that will lead to the liquid structure change which may include the altering of bonds style, the nearest neighbour distance, the first coordination number, etc., thus affect n_e and L_0, and result in the anomalous changes of resistivity, which reveal the TI-LLSTs.

The liquid structure of Sn has been investigated by neutron scattering experiments [30]. The experimental result shows that an obvious shoulder exists on the high-Q side of the first peak of $S(Q)$ at 573 K, 773 K, and even 1873 K. Since the shoulder is a sign of a covalent bond, these features for liquid Sn suggest that some tetrahedral SROs with covalent characteristics may remain in liquid Sn at lower temperatures, and at least the fragments of tetrahedral unit could persist at high temperatures in liquid Sn. So it can be logically assumed that it is the tetrahedral SROs with covalent characteristics in liquid Sn that mainly cause the reversibility of the TI-LLSTs. In addition, investigations of the high-temperature properties and SROs of melts show that the microheterogeneous states are metastable or nonequilibrium rather than thermodynamically stable [31]. In respect to the partial reversibility of the resistivity anomalous change in first heating cycle for Sn-Cu-Bi melts, it is reasonable to put forward the following assumption: there are two types of SROs in the first heating cycle in Sn-Cu-Bi melts, one is the irreversible metastable SROs, and the other is the reversible tetrahedral SROs with covalent characteristics, i.e. Sn-X SROs, such as Sn-Sn, Sn-Bi, and Sn-Cu. When the Sn-Cu-Bi melts are heated to the turning points in the first cycle heating, two types of SROs are broken up simultaneously or successively. The metastable SROs are broken into stable SROs that cause L_0 to decrease quickly, and result in a rapid increase of the resistivities of the Sn-Cu-Bi melts. The reversible Sn-X SROs with covalent characteristics are broken into smaller ones or dissolve and release more free electrons, which cause n_e increase and lead to the resistivities decrease or rise slowly with temperature increasing. Then only the fragments of Sn-X SROs with covalent characteristics remain in the melts in the high temperature melts. The remaining Sn-X SROs will rebuild and break again in the subsequent cooling and heating process, which causes the reversibility of TI-LLSTs in the liquid Sn and Sn-Cu-Bi alloys.

In addition, different content of Bi in Sn-Cu-Bi melts has various turning temperatures and characteristics of TI-LLSTs, which indicate that the type, amount, and size of SROs have a great effect on the TI-LLSTs. Therefore, TI-LLST in Sn-Cu-Bi melts is very complicated, and it needs further structural exploration by other techniques to probe the inherent nature of TI-LLST.

4. Conclusions

Based on the ρ-T curves of Sn-0.7Cu-xBi alloys with different content of Bi, anomalous changes of the resistivity can be observed at certain temperature ranges in two experimental cycles, which indicate TI-LLST occurs in Sn-Cu-Bi melts, and the possible TI-LLST is reversible after the first cycle heating.

Comparing the ρ-T curves of Sn-Cu-Bi melts with those of liquid Sn, Cu-Sb, and Bi, it can be inferred that the reversibility of TI-LLST in Sn-Cu-Bi melts is closely related to Sn or Cu. In addition, different content of Bi has a noticeable influence on the turning temperatures and characteristics of TI-LLSTs in Sn--Cu-Bi melts.

The short-range orders, derived from the corresponding crystal state, break into another one or dissolve into a more disordered structure at the turning point, which causes the unusual change of the resistivity in Sn-Cu-Bi melts. There may exist two kinds of TI-LLSTs in the first heating cycle in liquid Sn and Sn-Cu-Bi alloys: one is the metastable SROs breaking into stable SROs, which is irreversible; the other is the tetrahedral Sn-X SROs with covalent characteristic breaking on heating and rebuilding on subsequent cooling process, which leads to the reversible TI-LLSTs.

Acknowledgements

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