Electrical Resistivity and Structure of Cu-Pb Alloy during Cooling Process

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Abstract. The variations of electrical resistivity and cooling curve for monotectic Cu-Pb alloy have been measured from liquid state to ambient temperature. The structural transitions were discussed during cooling process. And the correlations between the variations of electrical resistivity, heat and structural transitions were also investigated. The linear relationship between the electrical resistivity and temperature curves in liquid state means there is no structural change in liquid Cu-Pb alloy. And during the solidification process, the electrical resistivity and cooling curves change with the occurrence of new phases.

Keywords. Electrical resistivity, structural transition, Cu-Pb alloy, liquid state.

1. Introduction
Monotectic alloy is an important class of alloy for its excellent physical, chemical and mechanical properties, which has a miscibility gap in binary phase diagram [1-2]. Cu-Pb alloy is a typical monotectic alloy, which shows a miscibility gap from 15 to 65 at% lead. Cu-Pb alloy has a wide field of application with good prospects in aerospace, micro-electronics or other relational industry [3-7]. So it is very important to learn the properties and structure of Cu-Pb monotectic alloy. For the large difference in density of pure Cu and Pb element, there usually is phase shift for Cu-Pb alloy during naturally cooling process. Many works focus in the phase shifts during cooling process and the solidification by deeply undercooled treatment [8]. Within the extended Faber-Ziman formalism which uses T matrix expressed in term of phase shifts, Chaïb interpreted the change of electrical resistivity of liquid Cu-Pb alloy accommodating change in components at certain temperature [9]. The electrical resistivity of liquid Cu-Pb alloy was mainly investigated in the miscibility gap concentration region before phase separation. Cui studied the microstructure evolution of Cu-Pb monotectic alloys during directional solidification. The absolute thermoelectric power has been studied for the system Cu-Pb from liquidus to 1100 °C [10].

And the behaviors of electrical resistivity for liquid Pb-Sn binary alloy have been investigated in the presence of ultrasonic field [11]. The previous research shows there is a liquid structural change in certain monotectic alloy, which lead to the segregation of solidifying structure [12]. And Xu investigated the electricity and mechanical properties of the rapid solidified CuPb alloy [13]. However, the structure and properties of Cu-Pb monotectic alloys was rarely reported during naturally cooling process.

The purpose of this work is to explore the change of structure and electrical resistivity of Cu-Pb monotectic alloy during naturally cooling process, which includes the liquid state, the miscibility gap concentration region and solid state.
2. Experimental Procedure

2.1. Preparation of Cu-Pb Alloy
The monotectic Cu-Pb (Cu-37.4%Pb) alloy was prepared by melting 99.99% Cu and 99.99% Pb in the high purity quartz crucible with a high-frequency induction furnace. The Cu-Pb alloy was heated to single liquid phase and held more than 5 min to be homogenized.

2.2. Measurement of Electrical Resistivity
With a homemade device, the electrical resistivity of melted sample is measured during the cooling process. The device is designed with the law of electromagnetic induction. The main measurement part likes the letter “C”. During the measurement, the melted sample was put into the device and cools naturally. The output signal of device change with decreasing temperature of sample, which revealed the relative change of electrical resistivity of sample with temperature by certain theory calculation. At the same time, the sample’s temperature was measured by an infrared high precision thermometer during cooling process.

3. Results and Discussion
The curves of electrical resistivity and temperature dependent on time are shown in figure 1. The changes of electrical resistivity and temperature for sample can be learned during cooling process.

![Figure 1. Curves of electrical resistivity and temperature dependent on time.](image)

3.1. Structural Transition of Cu-Pb Alloy
As we known, when there is a phase transition for sample, the heat has corresponding change which shows on cooling curve. So the change of cooling curve can reflect the structural transition of sample.

According to the phase diagram of Cu-Pb alloy, the solidification temperature of monotectic Cu-Pb alloy is 955 ℃ in theory. As shown in figure 1, there is a recalescence on the cooling curve. At the point of recalescence, the temperature of sample rebounded to 858 ℃ from 850 ℃. At this point, the monotectic phase transition occurred, e.g., L→L₁+α(Cu). The recalescence is for the heat release result from the nucleation and growing of L₁ and α(Cu) phase. With the further progress of monotectic transformation, when the heat from the nucleation and growing of new phases is equivalent with the heat lose to surrounding, the recalescence end and a temperature terrace occur on cooling curve. The remainder L liquid phase will transfer to L₁ and α(Cu) phase during the terrace progress. And the temperature terrace will end with the ending of monotectic transformation. However, the solidification do not end and it is the mixture of L₁ liquid phase and solid phase α(Cu). When the heat result from
the nucleation and growing of new phase can not remedy the heat lost in circumstance, the temperature of sample decrease again. It has been reported that one recalescence can be found when the subcooled temperature $\Delta T < 147K$, and two recalescence occurred as subcooled temperature $\Delta T=147-204K$ in the cooling curve [14]. When $\Delta T = 147-204K$, the first recalescence will be weak and the second recalescence will be very strong [14]. From the temperature curve in figure 1, the monotectic transformation occurred at 850℃, the subcooled temperature is about 105K and one recalescence can be found. The result is the same with the conclusions of Ref. [12]. When the sample cooled to about 304 ℃, the second terrace of temperature curve can be seen, which is the eutectic reaction, e.g., $L_1 \rightarrow \alpha(Cu) + Pb$. The solidification of samples ends at this time.

3.2. Electrical Resistivity of Cu-Pb Alloy
At room temperature, the electrical resistivity is 1.678 $\mu\Omega$·cm for pure Cu and 20.684 $\mu\Omega$·cm for pure Pb. As we known, the electrical resistivity is sensitive to the structure of materials, which is different for different structure.

In figure 1, it is can be found that the curve of electrical resistivity will change when there is variation on the temperature curve. It means there is structural change at these points which lead to the change of electrical resistivity of sample.

The dependence of electrical resistivity on temperature is shown in figure 2 for Cu-Pb alloy. When the temperature decrease to 850 ℃, 304 ℃ (point ‘A’ and ‘B’) respectively, and the electrical resistivity will change abruptly, which result from the structural change of sample. The points A and B divide the curve into three sections. The electrical resistivity will decrease with decreasing temperature and a linear relationship between temperature and electrical resistivity can be found in every section.

![Figure 2. Electrical resistivity of Cu-Pb alloy dependent on temperature](image)

It is considered that there is linear relationship between electrical resistivity and temperature for liquid metals [15], which is shown as:

$$R = aT + b$$  \hspace{1cm} (1)

where ‘a’ is the temperature coefficient of electrical resistivity, ‘$T$’ is the absolute temperature (K).

Combining figures 1 and 2, it is liquid state above 850 ℃ (A point) for Cu-Pb alloy. The linear relationship can be seen between electrical resistivity and temperature. And the electrical resistivity reduces with decreasing temperature. There is no abrupt change on curve, which can be considered that there is no structural change in liquid Cu-Pb alloy. The fitting linear relationship shows as below for liquid Cu-Pb alloy:

$$R = 1.25T-1915.3 \hspace{0.5cm} (850 \degree C \leq T \leq 1336 \degree C)$$  \hspace{1cm} (2)
where $R$ (a.u.) is electrical resistivity, $T$ (°C) is the temperature of Cu-Pb alloy.

When the temperature decreases to about 850 °C, the monotectic reaction occurred and the electrical resistivity decreased abruptly. The solid phase (Cu) separates out from liquid alloy during the monotectic reaction. (Cu) is a good electrical conductor, which increase the transmission capacity of electrons and decrease the electrical resistivity of Cu-Pb alloy. At the same time, for the larger Conductivity (Cu) of the collision probability of free electrons in (Cu) will be lower than that in liquid state. And when the free electrons in liquid alloy collide with (Cu), they will pass through (Cu) instead of scattering. These behaviors will increase free instance of free electrons, which lead to the larger Conductivity and lower electrical resistivity. The separation of new phase (Cu) will end with the end of monotectic reaction, the electrical resistivity will decrease with decreasing temperature and the slope of line (electrical resistivity dependence on temperature) will increase comparing with that in liquid alloy. When the temperature drops to eutectic temperature (e.g. 304 °C), L1→Pb+(Cu), the electrical resistivity decreases abruptly. For the eutectic composition (99.94%Pb) is very close to pure Pb, the separated Cu is little, which lead to small impact of Cu to the electrical resistivity of Cu-Pb alloy. Compared to solid alloy, atoms in liquid alloy will exit in disorder, which lead to the bigger probability of collision and scattering and smaller mean free path and then result in bigger electrical resistivity in liquid alloy. The content of operated Pb is larger and the electrical resistivity of solid Pb is smaller than liquid phase L1 while it is much smaller than that of solid pure Cu. So when the eutectic reaction begins, the electrical resistivity of sample decreases clearly. When the eutectic reaction ends, the solidification end and the sample become solid state totally. The electrical resistivity decreases with decreasing temperature.

4. Conclusion
The variations of electrical resistivity and structural transition for CuPb alloy were discussed during the cooling process. The linear relationship was found for electrical resistivity variations dependent on temperature in liquid, which shows there is no structural change in liquid state. At 850 °C, the electrical resistivity decreases abruptly for the monotectic action. And the electrical resistivity decreases clearly again for the eutectic reaction at 304°C. It shows the electrical resistivity change correspondingly when a new phase occurs.

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