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VISCOSITY, RESISTIVITY, AND STRUCTURAL CHANGES OF $Bi_{60}Ga_{40}$ ALLOY MELT WITH LIQUID-LIQUID PHASE SEPARATION

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Abstract. The temperature dependence of viscosity of liquid $Bi_{60}Ga_{40}$ alloy has been measured using torsional oscillation viscosity measurement. The results show that the change of viscosity with temperature is distinctly discontinuous, which can be divided into three parts: the changes in high temperature region, mid-temperature region, as well as low temperature region. In these different regions, the structures of melt are distinct. The viscous flow activation energy E and group size v_m in low-temperature zone, namely, the liquid-liquid phase separation zone are larger than those in the medium-temperature and high-temperature zone zone, and E and v_m in the medium-temperature zone is the smallest. There is only low temperature anomalous point on the resistivity-temperature curve in liquid-liquid phase separation zone. The appearance of exothermic peaks on DSC curve during cooling process further proved the structure changes of melt in 893K-923K. The liquid-liquid phase separation is naturally accompanied with structure change of melt in 535K-563K, which is also reflected by the discontinuous change of viscosity and DSC analysis.

1. INTRODUCTION

It is well known that phase transition in solid crystalline materials may occur under certain temperature and pressure. Some researches have found that the internal microstructure of metal melt tends to vary abnormally as its temperature changes [1,2].

Research on the structure of metals has attracted much more attention [3-5]. As the matrixes of solid crystalline and amorphous materials, melts impose significant impacts on the structure and properties of the generated solid materials by their structural changes [6]. The viscosity and resistivity are sensitive physical property parameters of melt structures, therefore, it is an effective research method for disclosing the liquid structure and the interaction between atoms.

In the present paper, we studied the viscosity and resistivity changes of $Bi_{60}Ga_{40}$ alloy at different temperatures between 1043K and the freezing point of the alloy melt. Further, the freezing behavior and structural change of the alloy within the liquid-liquid phase separation zone were discussed.

2. EXPERIMENTAL PROCEDURE

The samples for measuring viscosity and resistivity were taken from high-purity Bi and Ga with a weight percent over 99.9 wt.%, respectively. A high-temperature melt viscometer made by Japanese Industry Co., Ltd. was used to measure the alloy melt viscosity. The viscometer measurement ranges between 0 and 10 mPa·s with a measuring error less than 5%. Put the test piece into an earthenware crucible containing Al_2O_3. For each temperature

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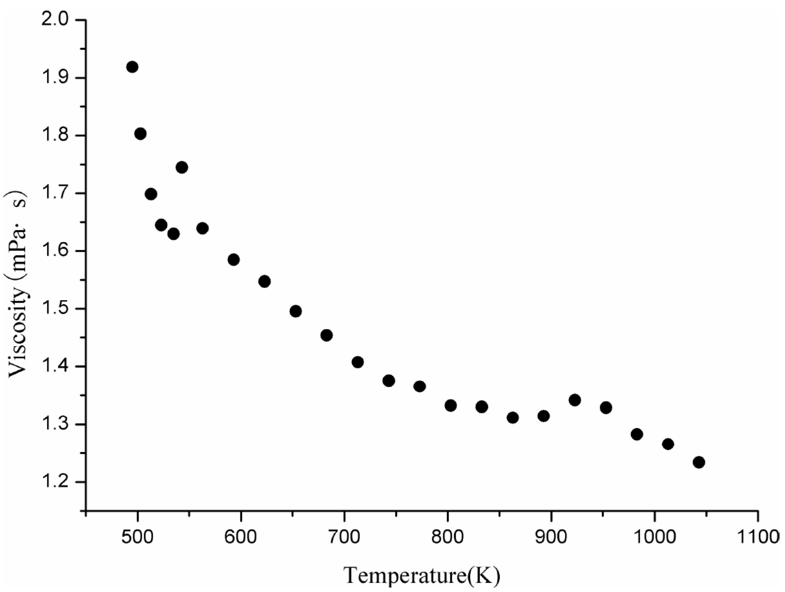

Fig. 1. Relationship between viscosities and temperature of $Bi_{60}Ga_{40}$ melt.

spot, measure the viscosity for 4-7 repeated times. The average of these repeated measurements will be the test piece viscosity at the temperature spot. Argon protection is used.

The resistivity of $Bi_{60}Ga_{40}$ alloy melt was measured with positive/negative DC electrode method [7], Then pour the mixture into a quartz crucible and insert a 1 mm tungsten filament measuring electrode. Use a KEITHLEY-2181 meter to measure the voltage and heat with a tube furnace during the test process. Argon protection is used .The heating and cooling rate is 2 K/min, respectively.

The DSC used in our experiments is 404DSC/3/4F-type, high-temperature differential scanning calorimeter manufactured by German Nczsch Co. with a measuring range from the room temperature to 1773K. Argon protection is used.

3. RESULTS AND DISCUSSIONS

In respect, with the relation between the viscosity and temperature of metal melt, Arrhenius equation [8] is widely accepted.

$$\eta = A\exp\left(E/RT\right), \tag{1}$$

where $A = h/v_m$; η –viscosity; h–Planck's constant; v_m–dimension of groups (atom, ion or cluster); R–gas constant; E–viscous flow activation energy; T–absolute temperature.

Determine the relation between $Bi_{60}Ga_{40}$ melt viscosity and temperature according to the test procedures above. Fig. 1 shows the viscosity change in the de-temperature process of $Bi_{60}Ga_{40}$ melt at 495K-1043K. $Bi_{60}Ga_{40}$ alloy melt exist liquid-liquid phase separation zone at 495K-535K. As indicated in Fig. 1, the $Bi_{60}Ga_{40}$ viscosity value increases roughly as the temperature decreases. However, the viscosity changes discontinuously at 893-923K. After an abrupt decrease, the viscosity value increases gradually with the temperature decrease. The viscosity increases sharply at 535-563K and the liquid-liquid phase separation of melt occurs. In the separation zone, the viscosity increases sharply as the melt temperature decreases. The relation of viscosity logarithm (lnη) and temperature reverse ($1/T$) can be typically represented by a straight line. Thus, the lnη-$1/T$ curve of metal melt $Bi_{60}Ga_{40}$ can be described in Fig. 2. The values of E and v_m can be determined by the slope and intercept of lnη-$1/T$ line (Fig. 2). From Fig.2, we see that the points are discretely distributed. There are three temperature zones including the high, medium and low-temperature zones. Each zone has a marked segment of temperature shock and the slope of one segment differs from another. The slope of the medium-temperature zone is smallest, the slope of the medium-temperature zone larger, and the slope of the low-temperature zone largest.

In each linear temperature zone, the viscosity observes Arrhenius law. The melt structure changes continuously in the same temperature zone. For different temperature zones, the straight slopes are different. This illustrates that the viscosity of each temperature zone corresponds to a different melt structure. Thus, it is possible that melt micro-

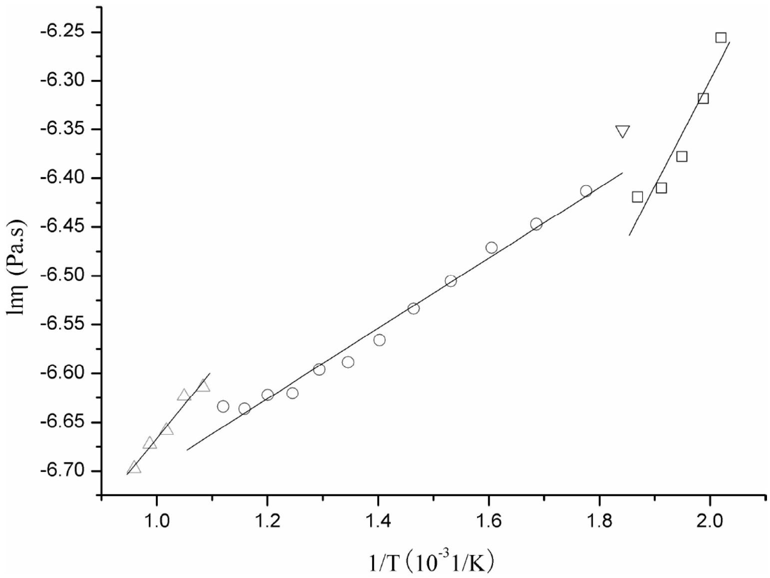

Fig. 2. Relationship between viscosity logarithm and temperature reciprocal of $Bi_{60}Ga_{40}$ melt.

structural mutation exists in the segment of temperature shock between two temperature zones.

E and v_m are useful parameters to denote the discontinuous structural change of the alloy melt. Since each straight segment in the lnη-1/T relation curve represents the viscosity change of liquid with certain group size (v_m), the dependency function between lnh and 1/T in each temperature zone can be obtained by linear regression analysis. This discloses the viscosity change of alloy melt $Bi_{60}Ga_{40}$ at different temperature. By linear regression analysis, we get

High-temperature zone:

$$\ln \eta = -7.35943 + 0.69308(1/T). \tag{2}$$

Medium-temperature zone:

$$\ln \eta = -7.04938 + 0.35429(1/T). \tag{3}$$

Low-temperature zone:

$$\ln \eta = -8.48120 + 1.09097(1/T). \tag{4}$$

The values of E and v_m of each temperature zone were determined with Eqs. (2), (3), and (4), we list them in Table 1. The variation of E indicates the difference of energy required by changing one flow state to another or, the difficulty in moving from an equilibrium position to another. The value of v_m represents the amount of particles (atom, ion or atomic group) aggregated inside the flow group. E and v_m are parameters related to melt microstructure and their variation indicates the change of melt structure. As seen from Table1, the values of E and v_m in low-temperature zone are the largest, while the values in medium-temperature zone are the smallest. The values of E and v_m in low-temperature zone are larger than those of the medium and high temperature zones. This illustrates that more activation energy will be needed when changing from heterologous to homogeneous flow group particles in the liquid phase separation zone, and it is hard to move.

Fig. 3 denotes the relation curve between the resistivity and temperature during the cooling process of $Bi_{60}Ga_{40}$ alloy. It shows that the resistivity decreases linearly with the temperature. When the temperature decreases to interval 533-489K, which represents the liquid phase separation zone, the alloy resistivity increases first and then decreases with the decrease of the temperature. At 527K, the

Table 1. v_m and E values of $Bi_{60}Ga_{40}$ melt at different temperature zones.

Parameters	High-temperature zone (893K-1043K)	Medium-temperature zone (535K-893K)	Low-temperature zone (495K-535K)
E/(kJ·mol^{-1})	5.762	2.995	9.071
v_m/10^{-25}cm^3	10.415	7.706	37.466

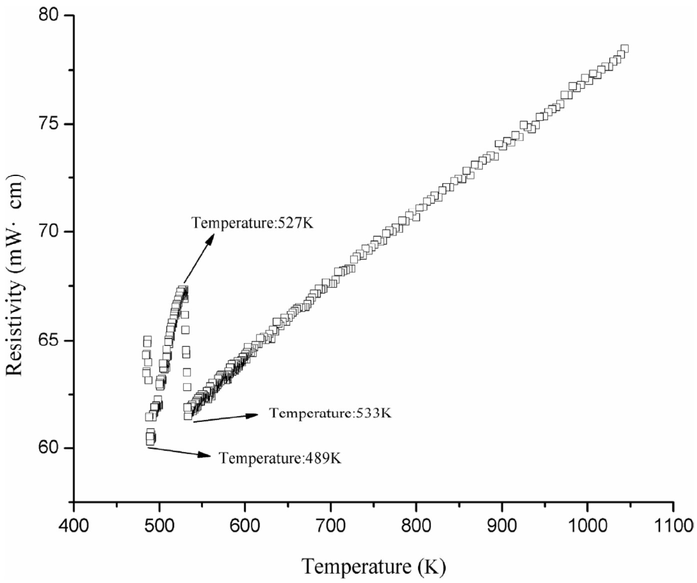

Fig. 3. Relationship between resistivity and temperature of $Bi_{60}Ga_{40}$ melt.

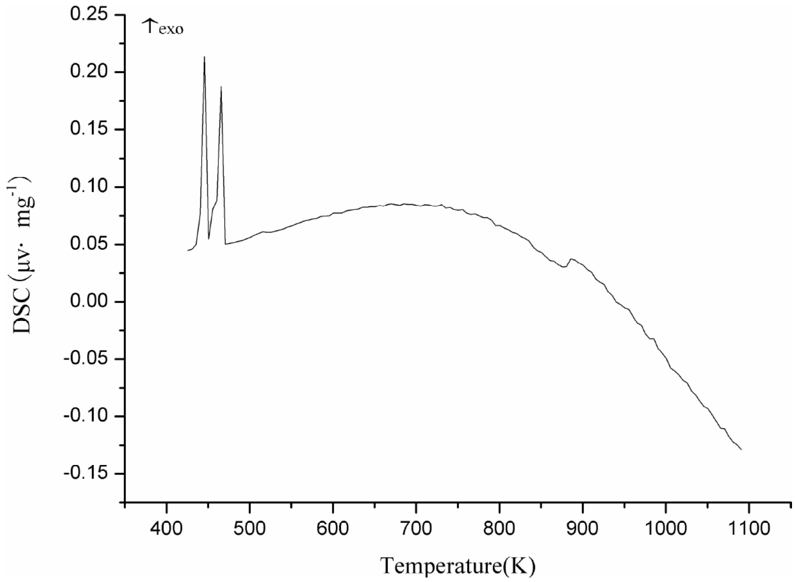

Fig. 4. DSC curve of $Bi_{60}Ga_{40}$ melt during cooling process.

resistivity reaches its maximum. This roughly agrees with the liquid phase separation zone in phase diagram. However, at the temperature interval 893-923K, the resistivity value does not change abnormally as the viscosity does.

The liquid phase separation of monotectic alloy is a complicated process. Based on the experimental results in literature [9] and the freezing process analysis of Bi-Ga monotectic alloy in liquid phase separation zone, we describe the liquid phase separation process of Bi-Ga monotectic alloy as follows. When the temperature decreases below 535K, large amount of Bi-Ga metallic bonds of Bi-Ga alloy melt break, and Bi-Bi and Ga-Ga covalent bonds forms. The binding force between atoms decreases immediately. This transformation causes the metal melt viscosity decreases slightly at 535K. With the decrease of the temperature, small amount of Bi and Ga phases nucleates by the fluctuation of energy and concentration. The nucleuses grow by diffusion and marangoni motion, and coarsen by collision and aggregation. When liquid drops of Bi and Ga phases reaches certain size, the second - phase Ga drops start to float under the density difference between constituents (the density of Bi is larger than that of Ga), and marangoni motion. The floating drops catch and aggregate other Ga drops. This leads the alloy to macrosegregation and results in lamellation of alloy melt. Ga phase with light mass aggregates on the top area of the sample.

This was proven by the experimental results in literature [10].

Fig. 4 shows the DSC curve with the decrease of $Bi_{60}Ga_{40}$ melt temperature, we can see a small exothermic peak around 883K. In the viscosity curve, the abnormal change of viscosity is at 893-923K. This roughly agrees with Fig. 4 and indicates that it is possible to have a structural mutation within the temperature zone. At 446K and 483K, there are two exothermic peaks. This proceeds slightly to the actual initial temperature of liquid phase separation and the temperature of monotectic reaction. One possible reason for this is the temperature lag caused by kinetic effect. Within a higher temperature interval of 893-923K, structural change of $Bi_{60}Ga_{40}$ melt by re-aggregation of atomic groups might occur. The structural change at 535-563K is caused by the change of the liquid-liquid phase separation.

4. SUMMARY

(1) The viscosity of alloy melt $Bi_{60}Ga_{40}$ changes discontinuously with the temperature. In terms of the viscosity change, the melt state falls into high, medium and low-temperature zones. A segment of temperature shock exists between temperature zones. The shock segments are 893-923K and 535-563K.

(2) The structure of melt $Bi_{60}Ga_{40}$ changes abruptly at 893-923K, and the liquid-liquid phase separation at 535-563K causes another structural mutation.

(3) The viscous flow activation energy E and group size v_m in low-temperature zone, namely, the liquid-liquid phase separation zone are larger than those in the medium-temperature and high-temperature zone zone, and E and v_m in the medium-temperature zone is the smallest.

(4) Roughly, the temperature zone of the liquid phase separation reflected by resistivity of alloy melt $Bi_{60}Ga_{40}$ corresponds to that in phase diagram. At 893-923K, the viscosity changes discontinuously and the melt resistivity does not change abnormally.

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