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Calorimetric study of Wood alloy[①]

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Abstract: The heat capacities of Wood alloy have been measured with an automatic adiabatic calorimeter over the temperature range of 80~ 360 K. The thermodynamic data of solid-liquid phase transition have been obtained from the heat capacity measurements. The melting temperature, enthalpy and entropy of fusion of the substance are 345.662 K, 18.47 $J\cdot g^{-1}$ and 0.053 43 $J\cdot g^{-1}\cdot K^{-1}$, respectively. The necessary thermal data are provided for the low temperature thermodynamic study of the alloy.

Key words: Wood alloys; calorimetry; heat capacity; melting points; fusion enthalpy **Document code: A**

1 INTRODUCTION

Wood alloy based on matrix of bismuth metal is a kind of alloy possessing low melting points and little rigidity. Its tensile stress is also very limited. Usually, it is used as temperature controlling materials to protect electric and steam equipment, such as, blown fuses and eutexia plugs. It is also applied in the alarming systems of modern automatic fire preventing equipment to detect fire, as well as automatic water spraying taps and fire preventing adjustive valves. As Wood alloy is solidifying, no obvious volume changes take place, and sizes of its product do not vary with temperature and pressure. So, Wood alloy can be used as molding mould and exact mould, as well as cathode coat of Ag, Co, Ni, Sn, and Zn for electroanalysis. Two kinds of common Wood alloy 50Bi-25Pb-12.5Sn-12.5Gd and 60Bi-16.7Pb-13.3Sn-10Cd have been reported, and their melting points are 344.15 K and 343.15 K[1~3] respectively. The melting points provided by reagent manuals are in the temperature range of 343~ 345 K[4].

Calorimetric studies of Wood alloy in low temperature range have not been carried out, and its thermodynamic data have not been reported. In order to expand its applied fields, reliable thermodynamic data are necessary. On the other hand, different ingredients have different thermodynamic parameters, in order to determine the thermodynamic data, such as heat capacities, melting points, enthalpy and entropy of fusion, the calorimetric study was carried out in our laboratory with an adiabatic calorimeter and a differential scanning calorimetric analysis (DSC), their results are presented in this paper.

2 EXPERIMENTAL

Samples of Wood alloy were produced by Shanghai reagents factory of No. 1, China. Its melting point ranges between 343~ 345 K.

The adiabatic calorimeter mainly includes a sample cell, equipped with an electric heater, and a thermometer, two adiabatic shields, two sets of differential thermocouples and a vacuum can[5~7].

The sample cell is a cylindrical container made of thin-walled (0.3 mm) gold-plated copper. It is 20 mm long and 20 mm in diameter with internal volume of 6 cm^3. Four L-shape radial gold-plated copper vanes of 0.10 mm thick are placed in the cell to speed up the thermal equilibrium. A heater made of d0.12 mm Karma wire is wound evenly on the surface of the cell to heat samples and container. At the bottom of the cell an Ω-shape sheath is silver-soldered for inserting a miniature platinum resistance thermometer. On the top of the cell, there is a flange, where the sealant would stick. The lid of the cell is made of gold-plated silver. A small amount of cyclo-weld is used to seal the lid to the main body of the sample cell. No leakage was observed as the sealed cell was kept in vacuum of 1×10^{-3} Pa over the temperature range of 60~ 360 K. At the center of the lid, there is a 5 cm long copper capillary for evacuating the cell, introducing the helium gas and hanging the sample cell. After introducing the helium gas the capillary is pinched off and the resultant fracture is soldered with a little amount of solder to ensure the sealing of the cell. To measure the temperature of the sample, a miniature platinum resistance thermometer was used (IPRT No2, R_0= 100 Ω, made in Shanghai), which was calibrated by the Station of Low-temperature Metrology and Measurements, Chinese Academy of Sciences. An integration digital multimeter (Model 5000, Sabstronics, Switzerland) was used to determine temperatures with an accuracy of 10^{-3} K.

The adiabatic control system consists of two adiabatic shields and a high vacuum can. The tempera-

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ture of the inner adiabatic shield was controlled as the same as that of the sample cell by an automatic adiabatic controller (Model ACD-79). Another temperature controller was used to dominate the temperature of the outer adiabatic shield, the temperature of which was controlled a bit lower than that of the inner one. The sample cell and adiabatic shields were sealed in the chromium-plated brass vacuum can, which was evacuated to 1×10^{-3} Pa by an oil diffusion pump system over the experiment. Thus the heat leakage by conduction, convection and radiation would be minimized to a very low level.

The energy introduced into the sample cell was supplied by a direct current power source, and can be calculated from the potential drops across the heater and a standard resistor connected in series with the heater. Heating intervals were controlled with a digital electronic timer. Potential drops were measured by digital multimeter. The potential drops across the platinum resistance thermometer and a standard resistor connected in series with the thermometer were measured with the same multimeter. The temperatures of sample cell were then calculated from the resistance of the platinum thermometer. All data including temperatures and energies were acquired and processed by a computer automatically. The temperature versus time curve of the calorimeter during the adiabatic calorimetric experiment is plotted in Fig. 1.

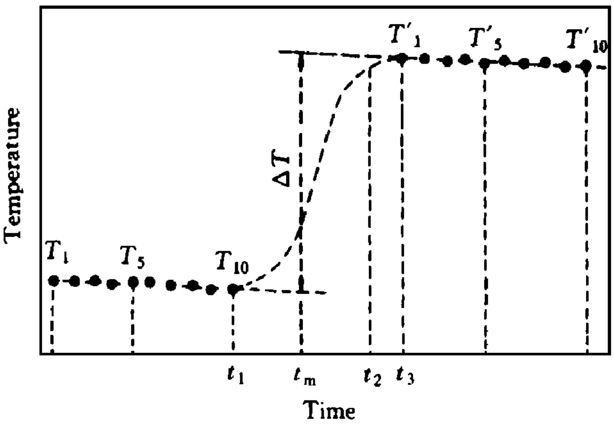

Fig. 1 Temperature—time curve of the calorimeter during the adiabatic calorimetric experiment

To verify the accuracy of the adiabatic calorimeter, molar heat capacities of the standard reference material α-Al_2O_3 were measured in the temperature of 60~ 360 K. The results indicate that deviations of the experiment data lie within ±0.2%, while the inaccuracy is within ±0.5% compared with the data of National Bureau of Standards[9].

Heat capacities were determined over the temperature range from 80 to 360 K with adiabatic calorimeter. The melting point and enthalpy of fusion can be obtained from the measuring heat capacities. The temperatures of initial melting and final melting can be derived from the c_p —T curve.

3 RESULTS AND DISCUSSION

3.1 Heat capacities

The heat capacities of Wood alloy were determined in the temperature range of 78~ 360 K. The measured data (78 points in total) are listed in Table 1 and demonstrate in Fig. 2 and Fig. 3. The result indicates that in the temperature range of 78~ 342 K and 351~ 360 K, Wood alloy is in solid state and liquid state respectively. Heat capacities versus temperatures curve are smooth in the two temperature ranges, which means that this material is stable in the experimental temperature region and there is no phase transition in solid and liquid state.

The following polynomial equation is obtained by least square curve fitting.

In the temperature range of 78~ 342 K (solid):

$$c_p/(\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}) = -0.09321 + 0.006388T - 7.029\times10^{-6}T^2 + 4.051\times10^{-8}T^3 - 1.080\times10^{-10}T^4 + 1.113\times10^{-12}T^5$$

correlation coefficient $R = 0.99756$.

In the temperature of 351~ 360 K (liquid):

$$c_p/(\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}) = -14.53 - 0.08783T + 1.635\times10^{-6}T^2$$

correlation coefficient $R = 0.99889$.

Table 1 Experimental heat capacities of Wood alloy

T/K	c_p	T/K	c_p	T/K	c_p	T/K	c_p
79.179	0.1201	152.969	0.1314	241.460	0.1460	330.387	0.1780
82.810	0.1203	156.697	0.1323	245.882	0.1463	334.587	0.1844
85.604	0.1215	160.811	0.1334	250.275	0.1465	338.638	0.1939
88.693	0.1217	165.102	0.1334	254.632	0.1469	342.492	0.2049
91.734	0.1221	169.372	0.1340	258.988	0.1473	344.855	0.9931
94.725	0.1226	173.612	0.1345	263.136	0.1482	345.489	3.5859
98.109	0.1239	177.817	0.1347	267.679	0.1490	345.641	28.559
101.864	0.1244	181.996	0.1349	271.987	0.1493	345.662	39.364
105.803	0.1254	186.150	0.1353	276.269	0.1506	345.678	27.763
109.816	0.1257	190.608	0.1368	280.531	0.1512	345.721	13.080
113.793	0.1273	195.365	0.1368	284.777	0.1520	345.832	5.5122
117.693	0.1274	200.092	0.1376	289.000	0.1532	346.303	1.9282
121.533	0.1278	204.800	0.1377	292.717	0.1542	347.496	1.0662
125.478	0.1289	209.490	0.1381	297.719	0.1557	349.369	0.7972
129.442	0.1284	214.150	0.1390	302.609	0.1586	351.887	0.5370
133.520	0.1292	182.777	0.1399	307.441	0.1607	354.710	0.5638
138.225	0.1301	223.221	0.1418	311.834	0.1627	357.409	0.5855
141.510	0.1302	227.613	0.1426	316.910	0.1641	360.209	0.6163
145.283	0.1296	232.511	0.1434	321.533	0.1680		
148.559	0.1310	237.301	0.1443	326.033	0.1726		

Note: Unit of c_p is J/(g·K).

3.2 Melting point and enthalpy of fusion

The melting point can be obtained with step-by-step heating based on the following equation[8]:

$$T_m = T'_i + [Q' - \overline{H}_0(T_f - T'_i) - mc_{p(L)}(T_f - T_m)]/mc_{p(S+L)}$$

where T_m is the melting point of the sample, T'_i the equilibrium temperature in the melting region, T_f the temperature a few degrees above the melting point, Q' the total heat energy introduced into the sample cell from T'_i to T_f, $\overline{H}_0$ the average heat capacity of sample cell from T'_i to T_f, $c_{p(L)}$ the heat

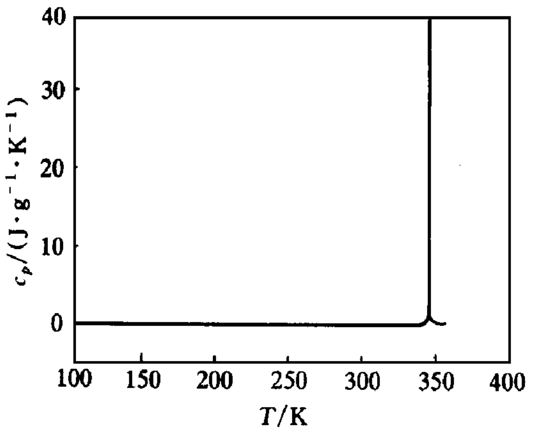

Fig. 2 Heat capacities of Wood alloy

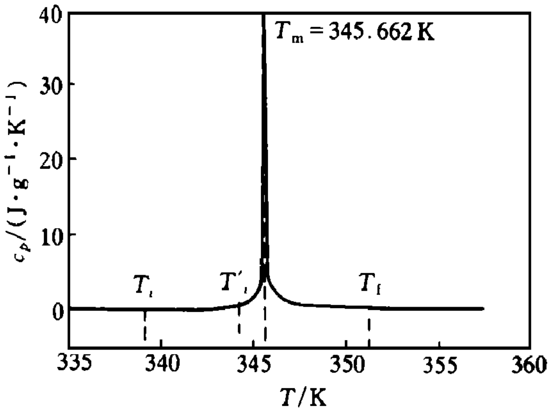

Fig. 3 c_p —T curve in melting process

capacity of the sample in liquid phase at $(T_f + T_m)/2$, $c_{p(S+L)}$ the heat capacity of liquid-solid two phase mixture at $(T_i + T_m)/2$, m the mass of the sample.

With 11 times heating and 3 series of repeating measurement in the melting region, the melting point of the sample, $T_m = 345.662\,\mathrm{K}$, is obtained.

The initial and final melting temperatures of the sample are 338.638 K and 351.887 K respectively. The sample exists in the two-phase state in the temperature range of 338.638~351.887 K. The enthalpy of fusion of the sample can be obtained as

$$\Delta H = \left[Q - \int_{T_i}^{T_f} m_{(S)} c_{p(S)} \mathrm{d}T - \int_{T_i}^{T_f} m_{(L)} c_{p(L)} \mathrm{d}T - \int_{T_i}^{T_f} H_0 \mathrm{d}T \right] / m$$

where T_i is a temperature a few degrees lower than the initial melting temperature, Q the total energy introduced into the sample cell from T_i to T_f, m the total mass of the sample, $m_{(S)}$ the sample mass in solid phase, $m_{(L)}$ the sample mass in liquid phase.

In fact, the following equation is used to calculate the enthalpy of fusion, owing to the difficulty of the determination of the $m_{(S)}$ and $m_{(L)}$:

$$\Delta H = \left[Q - m \int_{T_i}^{T_m} c_{p(S)} \mathrm{d}T - m \int_{T_m}^{T_f} c_{p(L)} \mathrm{d}T - \int_{T_i}^{T_f} H_0 \mathrm{d}T \right] / m$$

Finally, the enthalpy and entropy of fusion of the sample are determined to be 18.47 $\mathrm{J\cdot g^{-1}}$ and 0.05343 $\mathrm{J\cdot g^{-1}\cdot K^{-1}}$, respectively.

4 DSC RESULTS

A differential scanning calorimeter (TA Instrument DSC 910 s) was used to conduct the thermal analysis of Wood alloy. The heating rate was 5 K/min and experimental atmosphere was nitrogen gas. The melting peak was observed at 346.27 K with three times repeating and the enthalpy of fusion of the sample was determined to be 19.1 $\mathrm{J\cdot g^{-1}}$.

The melting point of Wood alloy sample determined by DSC accords well with that obtained by adiabatic calorimetry. As the way DSC getting data of heat capacities is dynamic scanning, it leads to lower accuracy than that of the adiabatic calorimetric method. The heat capacities of Wood alloy determined by the present investigation provide an important foundation for the study of the thermodynamic properties of this alloy at in low temperature.

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