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Lead–tin solder characterization by differential scanning calorimetry

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Abstract

The electrolytic deposition of chromium on the bore of thick walled high pressure cylinders uses a lead–tin alloy as the anode for the plating process. The anode is prepared by melting a lead–tin solder over a cylindrical copper core, which is then machined to the proper diameter. Using differential scanning calorimetry, the melting temperature of various ratios of lead–tin can be measured and a portion of the phase diagram can be established between the solid and liquid states. The melting temperature of a solder can then be measured and the composition can be obtained from the phase diagram. Published by Elsevier Science B.V.

Keywords: Lead–tin solder; Differential scanning calorimetry; Emission spectroscopy

1. Introduction

A binary alloy of lead and tin is commonly used as an anode for the electro-deposition of chrome on a metal surface. The alloy used as the anode in the electro-deposition of hard chrome on a substrate should range between 90 and 95% lead with the remainder tin. Emission spectroscopy is frequently used as an analytical method to verify the composition. To analyze samples by emission spectroscopy requires the acid digestion of solid samples with nitric acid, and then the addition of a high concentration of hydrochloric acid to redissolve the tin. However, frequently all the tin will not go back into solution depending on the weight percent of tin present. The ability to digest and keep both the lead and tin in solution makes the analysis very difficult. Occasionally, the tin has to be precipitated, filtered, burned in a muffle oven and weighed as an oxide. This is a very tedious and time consuming process.

An alternate method of analysis utilizes differential scanning calorimeter (DSC) to melt the sample and the onset temperature and enthalpy of melting are measured. Lead and tin form a binary alloy. From the phase diagram, as the lead composition decreases from 100%, the alloy melting temperature falls until it reaches the eutectic temperature. Thus, by measuring either the melting temperature or the melting enthalpy of the liquid + alpha transition to all liquid, one can determine the composition of the binary alloy. The method is faster and requires little sample preparation.

2. Experimental

Samples were prepared using pure lead and tin. The samples used to prepare a calibration curve varied from 100% lead and 0.00% tin to 76.97% lead and

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23.03% tin. The lead used to prepare the standard calibration curve was reagent grade lead sticks from Matheson, Coleman and Bell. The tin was purchased from Perkin-Elmer Corporation's catalogue of DSC reference materials certified as 99.99% pure.

To prepare the various calibration samples, the lead sticks were cut into thin slabs using a razor blade to expose two fresh surfaces free of oxide. A rectangular segment of the slab was cut from the center to ensure that no oxide was present, then the specimen was weighed. A section of the tin reference material was cut using a separate razor blade (oxide formation was not a problem with the tin), weighed and then placed on top of the flat lead section in an aluminum pan. The open pan was placed in a Perkin-Elmer DSC-7 in the sample cell and a open blank aluminum pan placed in the reference cell. The DSC was allowed to purge with nitrogen for 10 min prior to rapidly heating the sample to 400°C. The sample was held at a temperature for 10 min and then rapidly cooled to 50°C. The sample was then heated at 10°C/min from 50 to 350°C. The heat flow versus temperature was recorded.

Each calibration sample and anode sample were analyzed in triplicate. The onset temperature of melting, peak temperature and enthalpy of melting were measured and recorded for the alpha + liquid to liquid transition for the binary alloy.

3. Results

As seen in Fig. 1, the binary alloy phase diagram for lead–tin, the melting temperature for the alloy varies between 327°C for pure lead and 232°C for pure tin. At the eutectic point, 62% tin and 38% lead with a melting temperature of 183°C, to the melting temperature for pure lead, 327°C, as we move along the phase boundary between the alpha + liquid and liquid line the melting temperature increases with increasing lead concentration. In the range of interest, 85% lead and 15% tin to pure lead, the alpha solid partially melts going to liquid + alpha. On further heating, the remaining alpha solid melts.

Fig. 2 is a typical DSC scan for the binary melting of lead–tin. From the phase diagram, it can be seen that as the temperature increases, below 19% tin, the alpha + beta solid goes to all alpha solid. Above 19% tin, the alpha + beta solid goes to alpha + liquid. As the temperature continues to increase, below 19% tin, some of the alpha solid melts. Eventually, the remaining alpha solid goes to liquid. Examining the melting peak, a shoulder can be seen on the left side of the peak revealing the overlapping of two peaks. The first peak or shoulder is the partial melting of the alpha solid and the second peak is the melting of the remaining alpha solid. Thus, the area under the melting peak is a composite of the enthalpy for the partial melting of the alpha solid going to alpha + liquid and the complete melting of the remaining alpha in the alpha + liquid region.

In Table 1, the binary alloy composition, onset of melting temperature, melting enthalpy and peak melting temperature for a series of high purity lead–tin alloys can be seen. Comparing the temperatures along the liquidus curve in the phase diagram with the onset

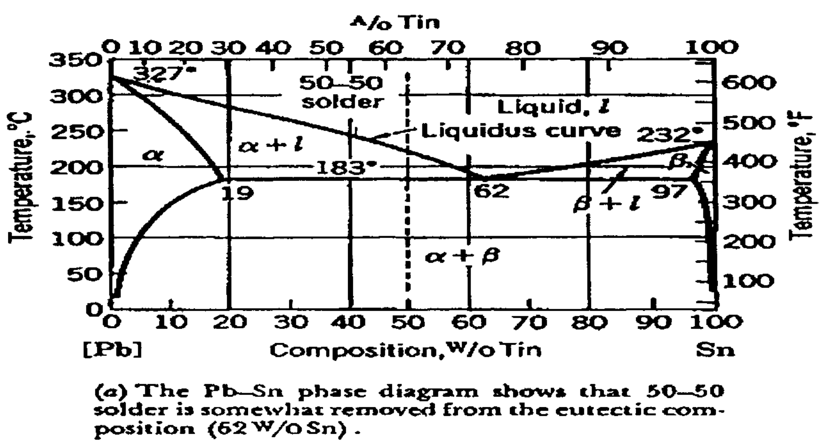

Fig. 1. Lead–tin phase diagram.

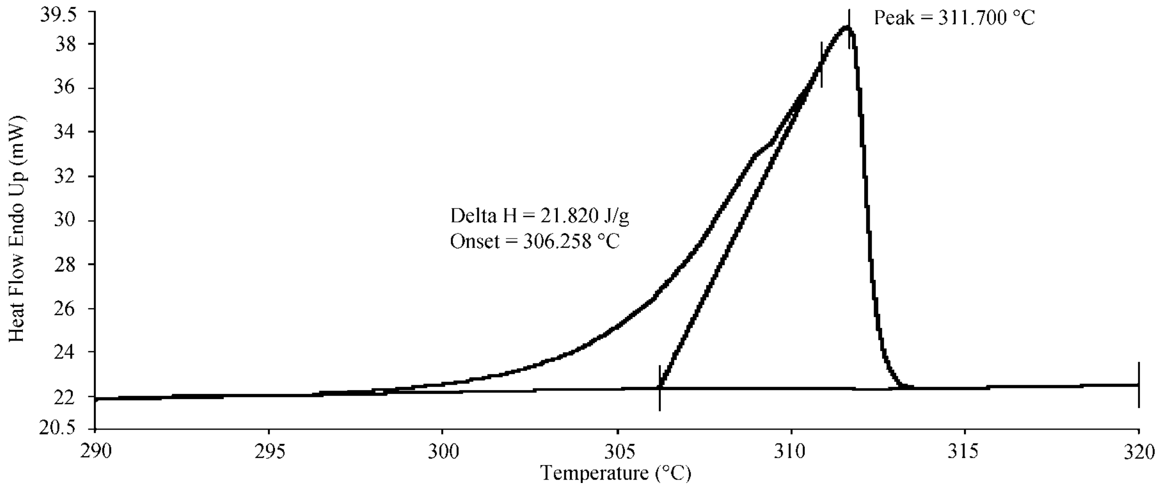

Fig. 2. DSC scan for alloy 94.27% lead–5.73% tin.

of melting temperature in the table, it can be seen that the values in the table fall below the liquidus curve, while the peak temperatures show good agreement with the liquidus curve. This is probably due to the inability of the DSC to resolve the alpha to alpha + liquid transition from the alpha + liquid to all liquid transition.

Looking at Fig. 3, the onset of melting for the alpha + liquid transition to all liquid was plotted versus the weight percent of lead in the samples. As the percentage of tin increases, the melting temperature of the binary alloy decreases. Over the range of 0–23.03% tin, the onset melting temperature decreased by 67.38°C. A sample of a typical lead–tin solder used to prepare a plating anode was analyzed using the calibration curve plotted in Fig. 3. The sample had a melting onset temperature of 303.0°C and an enthalpy of 22.09 J/g. From the calibration curve, a melting temperature of 303.0°C corresponds to a composition of 93.5% lead and 6.5% tin.

In Fig. 4, the enthalpy of melting was plotted versus the weight percent of lead in the samples. In the range of 92.5–100% lead, the rate of change or slope of the curve is small, resulting in a small change in the melting enthalpy over a large portion of the curve in the region of interest. A change of less than 2 J/g was observed, while the lead concentration varied by 7.5%. Thus, the sensitivity to small changes in the

Table 1
DSC results for lead/tin binary alloy

Pb (%)	Sn (%)	Weight (mg)	Onset temperature (°C)	Enthalpy (J/g)	Peak temperature (°C)
100.00	0.00	20.38	325.87	23.07	328.41
97.17	2.86	24.83	316.70	22.60	319.81
96.89	3.11	23.08	316.48	22.69	320.81
94.80	5.20	18.79	308.35	21.61	313.48
94.27	5.73	21.30	305.39	21.92	311.81
92.66	7.34	24.80	302.37	22.63	308.57
91.96	8.04	23.13	297.84	21.23	304.48
89.98	10.02	19.96	289.95	21.03	299.92
89.05	10.95	24.84	286.23	20.37	296.97
82.04	17.96	24.33	260.49	16.29	278.81
76.97	23.03	25.71	258.49	16.10	279.03

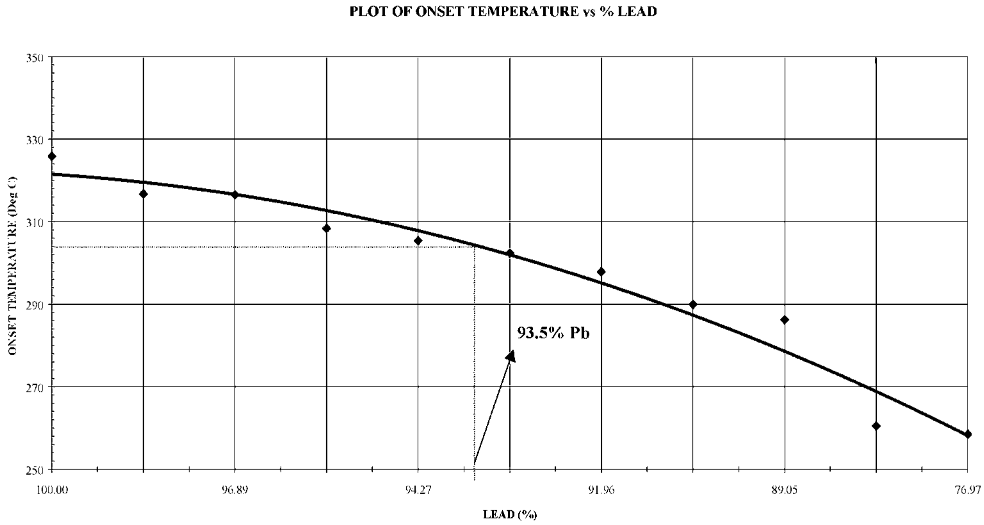

Fig. 3. Plot of onset of melting versus binary alloy composition.

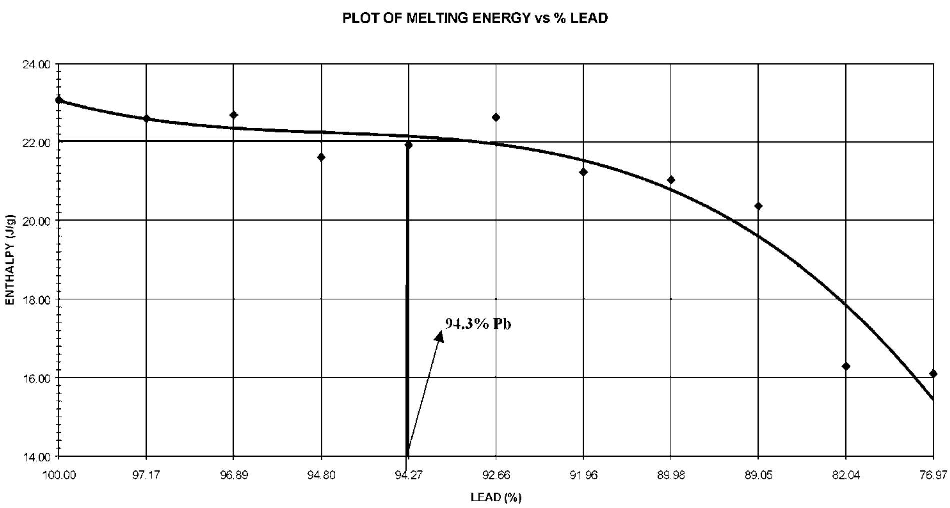

Fig. 4. Plot of the enthalpy versus binary alloy composition.

lead–tin concentration in this range is difficult to detect. Looking at the calibration curve in Fig. 4, the lead–tin composition for the anode sample was calculated to be 94.3% lead and 5.7% tin. This is a significant difference from the 93.5% lead and 6.5% tin concentration obtained for the melting point data. As a matter of fact with a standard deviation of ±0.22 J/g in the sample, the lead concentration can vary from approximately 93 to 95% lead.

4. Conclusion

Differential scanning calorimetry provides an alternative method of analysis for the determination of a binary alloy composition of lead–tin. Compared to inductively coupled plasma emission spectroscopy, it provides a faster method of analysis with very little sample preparation. The use of the onset melting temperature appears to be a more accurate method to determine the lead–tin composition in the region of 0–7.0% tin, then the melting enthalpy, due to the small change observed in the melting enthalpy over that portion of the curve. However, caution should be used when applying this method to insure that the alloy does not contain any other alloying elements that could effect the sample melting temperature and enthalpy.