APPLICATION NOTE

Simultaneous Thermal Analysis

Authors

Bruce Cassel

Kevin P. Menard

PerkinElmer, Inc.
Shelton, CT USA

Professor Charles Earnest

Berry College
Department of Chemistry
Mount Berry, GA USA

Use of the STA 8000 Simultaneous Thermal Analyzer for Melt Analysis of Alloys

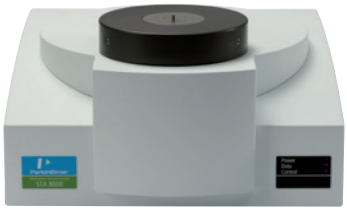

Figure 1. STA 8000 Simultaneous Thermal Analyzer.

Introduction

While determining the composition of alloys has traditionally been the domain of differential scanning calorimeters or differential thermal analyzers,[1] the STA 8000 has shown itself to be capable of this type of demanding analysis as well. The requirements for melt analysis are accurate temperature and melt energy measurement and the ability to exclude oxygen – or if necessary, nitrogen – during the analysis. This note shows examples of two high temperature melting systems, including iron-nickel alloys which require oxygen exclusion.

Experimental

The STA 8000 (Figure 1) provides the analysis of sample sizes typically in the 10 to 200 milligram range with the samples heated by a small furnace (~20 cc volume) capable of operating from 15 to 1600 degrees Celsius.[2] The STA sensor is a double pan differential temperature sensor which is calibrated to generate data for heat flow to the sample with an accuracy of 5% or better. The weight sensor is located remotely below the furnace where it is isolated from sample decomposition products by inert purge through a narrow channel. This provides microgram-level weight change detectability of sample loss or oxidative gain. Unless otherwise noted the purge gas used for this note was nitrogen at a flow rate of 100 cc/min. The use of argon instead of nitrogen is supported in the Pyris™ software which controls the flow rate of gas through the furnace chamber and provides for gas switching and flow rate changes.

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The samples chosen for analysis included elemental materials of high purity and industrial samples of uncertain composition. The two component phase diagrams for these systems (which indicate the solidus and liquidus temperatures versus composition) are well documented in the literature, so that a determination of the melting onset from the thermal curve is sufficient to determine the composition. Conversely, the analyzer can be used to generate the phase diagram for accurately prepared, multiple component alloy systems.

Results

Gold-Copper Alloys. With applicability to jewelry production, dental fillings, aerospace, and especially electronics, the gold-copper alloy is used as a reliable braising system to bond metallic surfaces or as an inert coating. The materials whose STA data is shown in Figure 2 were produced by weighing out reagent copper granules and 99.99% purity gold wire into the STA pan, then heating the mixture and holding isothermally above the gold melting point to allow alloy formation. The alloy was then cooled, then analyzed in the STA, all these steps being part of one analytical method using Pyris Software. As can be seen from Figure 2, small increases in the copper content result in significant changes in the melting point. Thus the STA, which has a temperature accuracy specification of better than a degree, is able to determine the composition of a material in a known alloy family. The two-component phase diagram for this system taken from the literature[4] is shown in Figure 3 with the placement of the data points (marked by vertical slashes, not to be taken as error bars).

The extrapolated onset temperature from the leading edge of the DTA thermal curve can be taken as the determination of the solidus, the onset of melting when heating the solid solution. In compositions where there is a melting range, *i.e.,* where the liquidus is measurably higher than the solidus, the liquidus can be taken as the alloy melting peak

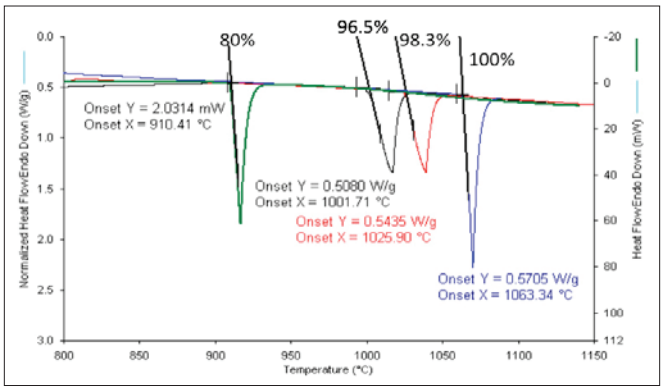

Figure 2. Melting endotherms for gold and three gold-copper alloys.

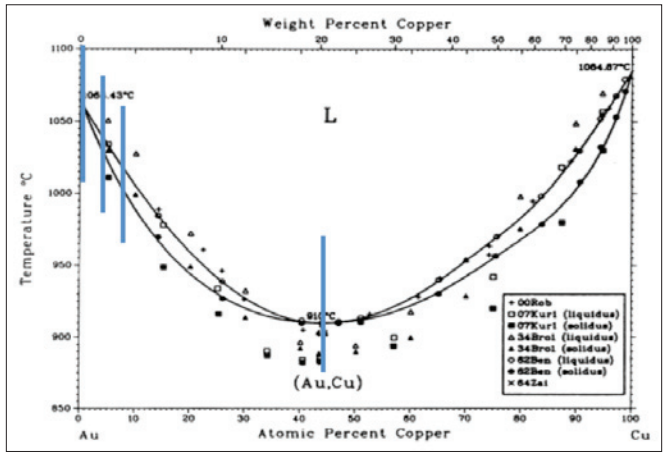

Figure 3. Gold-copper phase diagram showing compositions of endotherms in Figure 2.

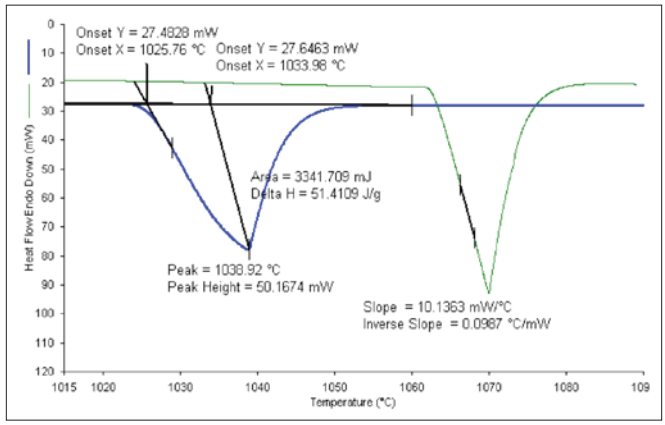

Figure 4. Determination of solidus and liquidus (1.7% Cu: 98.3% Au sample). The slope calculation from the gold melt (the higher temperature peak) allows lag correction for the peak parameter of the alloy.

temperature after correcting for thermal lag. This is done by using the slope of the leading edge of the DTA thermal curve of the pure primary component (Figure 4). The peak of the observed melting endotherm is the point at which the last of the solid material melts; however, since the latent heat of melting causes the temperature of the sample to lag behind the sensor, the peak maximum should be corrected for this effect. This thermal lag can be evaluated from the melting peak of a high purity sample, since when it is melting, the temperature of the sample remains constant at the melting point until all the sample has melted. Since the furnace temperature is increasing linearly, the leading edge of the peak should be linear. Notice that the peak shape for pure gold is linear and faithfully follows the theoretical shape expected from melting in a quantitative calorimeter. The inverse slope of that leading edge is just the ratio of apparent temperature change per unit heat flow change. Thus, the solidus of the alloy is seen to be the peak temperature minus the product of its peak height and the inverse slope (as calculated using Pyris software) of the leading edge of the melt of the pure material. The results obtained were in excellent agreement with literature.[5]

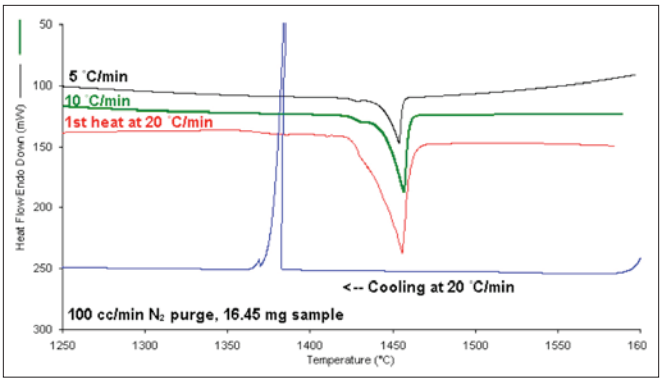

Figure 5. Invar36 at three heating rates, and cooling.

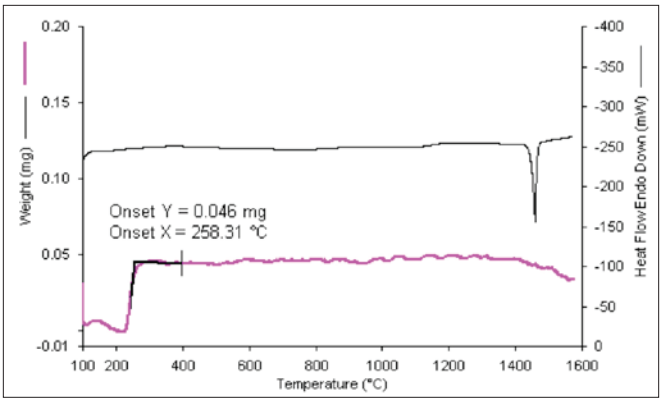

Figure 6. Invar36 alloy at 10 °C/min showing the melt and the step up in apparent weight at the Curie temperature.

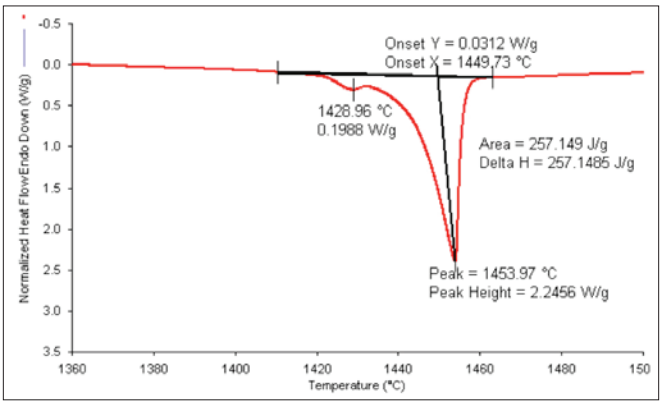

Figure 7. Invar 36 at 5 °C/min showing values of the liquidus and solidus.

Invar and Other Iron-Nickel Alloys. The Invar alloys of Iron and nickel have uniquely low coefficients of expansion which make them useful in fine watches, sensitive instrumentation, aerospace and especially in electronic applications where small differences in expansion may cause failure. A sample of Invar 36 (36% nickel) was obtained from the PerkinElmer manufacturing group where it is used in construction in analytical instruments. The sample was analyzed in the STA 8000 at 20, 10 and 5 °C/min using a sample purge of 100 cc/min nitrogen. The resulting thermal curve can be seen in Figure 5. Using a strong magnet over the STA furnace allowed the Curie temperature (the temperature above which all attraction to a magnet disappears), to be recorded (Figure 6). At the end of the analysis the weight of the Invar sample was determined to not have changed by more than two tenths of a percent, an indication that any oxidation from back diffusion from air into the exit port was minimal at this purge rate. Figure 7 shows the DTA thermal curve for Invar when heated at 5 °C/min. This rate allows a better resolution of the solidus and liquidus, which were calculated from the peak maxima and corrected using the leading edge slope of melting reagent iron.

Summary

The STA 8000 is designed to give accurate melting characteristics over a temperature range from ambient to 1600 °C. The quality of the calorimetry is sufficient to allow quantitative corrections for thermal lag as is normally done in a differential scanning calorimeter. Using a purge rate of 100 cc/min of house nitrogen there was sufficient oxygen exclusion to limit oxidation of iron and iron alloys to less than 0.2% of original weight after extended analysis to 1600 °C. The use of argon purge and faster, or slower, purge rates is also supported. This should qualify the STA 8000 for quantitative characterization of alloy systems up to 1600 °C. Examples of using a DTA approach to characterize ternary alloy systems can also be found in the literature.[6,7]

References

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3. STA Brochure # 010452_01.

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5. M.H. Sloboda, Gold Bulletin 1971 Vol. 4, No. 1, Chamber of Mines of So. Africa. Pub.

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PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

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