**A small sealed Ta crucible for thermal analysis of volatile metallic samples**

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Differential thermal analysis on metallic alloys containing volatile elements can be highly problematic. Here we show how measurements can be performed in commercial, small-sample, equipment without modification. This is achieved by using a sealed Ta crucible, easily fabricated from Ta tubing and sealed in a standard arc furnace. The crucible performance is demonstrated by measurements on a mixture of Mg and MgB₂, after heating up to 1470°C. We also show data, measured on an alloy with composition Gd₄₀Mg₆₀, that clearly shows both the liquidus and a peritectic, and is consistent with published phase diagram data.

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Differential thermal analysis (DTA) is an important tool for determining both phase-diagram and thermal-processing information for advanced-materials development. It is particularly helpful in the solution growth of single crystals. For a typical commercial, small-sample, DTA, in this case a PerkinElmer Pyris DTA 7, the standard crucible is an open Al₂O₃ crucible. This presents two problems, one of stability and one of volatility. To close the crucibles, Al₂O₃ caps are available, but they do not provide sufficient sealing for samples containing highly volatile components. In addition, elements such as Li, Mg, and rare earths attack Al₂O₃.

For metallic alloys that do not attack it, Ta is often the crucible material of choice. Ta is easily fabricated into crucibles and has been found to remain inert during lengthy high-temperature growth experiments for a wide range of metallic alloys. Moreover, in growth crucibles, Ta caps can be welded onto the crucibles in a standard arc furnace, resulting in a sealed crucible with an Ar room temperature pressure of ~1 bar. For growth of crystals that involves volatile elements, such as Mg, Li or Yb, such sealed Ta crucibles have been shown to yield well-formed single crystals. In order to replicate the growth environment, small sealed Ta crucibles, usable in a commercial DTA, are required. Given the high melting point of Ta, ~3000°C, and the small dimensions of the crucible, careful consideration must be given to the heat flow during the sealing process.

In the differential thermal analyzer, Al₂O₃ crucibles are placed in Pt sample and reference cups with Pt-based thermocouples inserted through the bottom so that they contact the crucibles. If Ta is placed in direct contact with the Pt, there is a possibility that at elevated temperatures (∼1000°C), Ta may diffuse into the Pt, and thereby change the thermocouple calibration, or it may create a diffusion bond between the Pt parts and the Ta. Therefore, the Ta crucibles are placed inside the standard Al₂O₃ crucibles, which can be reused multiple times in this application.

The body of the crucible consists of small-diameter Ta tubing. In order to successfully seal volatile metals in such a crucible, it is necessary to keep their temperature as low as possible. However, the radiant heat produced while sealing the crucible was found to be sufficient to volatilize Mg. The incorporation of a radiation shield inside of the crucible adequately addressed this problem.

In Fig. 1 the components of the crucible (a-h) are displayed. The Ta crucibles are made of pieces of Ta tubing 10-12 mm length, 2.15 mm inner diameter and 3.2 mm outer diameter (b). Two pieces of Ta of about 120 mg and another one of about 75 mg are melted in a standard Ar-atmosphere standard arc furnace, to make Ta balls, which form naturally upon melting, because of surface tension. The larger two balls (a and e), are larger than the inner diameter of the Ta tube and are used to form the ends of the crucible, whereas the smaller ball (d), which just fits inside the tubing, will act as a radiation shield that protects the sample (c).

To form an unsealed Ta crucible, the Ta tube (b) is clamped in the water-cooled copper hearth of an Ar-atmosphere standard arc furnace, and one of the larger Ta balls (a) is placed on top of it. The ball is carefully
melted (with a low operating current), so that it forms a closed lid of the crucible without making it wider than the original tube. This crucible is the standard Ta crucible that we have used before. A similar crucible can be made by mounting the tubing in a lathe and spinning one end closed, but this requires a skilled machinist, and can thin the walls and leave a small hole at the tip.

Next, the sample (c) is placed inside, and a pair of cutters is used to pinch indentations in the crucible (f). The purpose of the indentations is to position the radiation shield (d), the smaller Ta ball, above the sample so that the shield is in contact with the crucible but with neither the sample nor the lid (e). The assembly is then sealed by carefully melting the lid, the second larger Ta ball, on top of the crucible, as above, to form the sealed crucible (h). Finally, the standard Al$_2$O$_3$ crucible (g) will hold the crucible in the DTA.

We have made no attempt to accurately determine the maximum sample temperature as the crucible is sealed with the radiation shield in place. However, we have used this technique to encapsulate several pieces of Mg and then opened the crucible to inspect the contents. The results indicated that partial melting of some of the Mg pieces occurred, but the pieces were still distinct. This suggests that, although there was sufficient radiative heat to bring the irregular pieces of Mg to near their melting temperature, upon the occurrence of surface melting, the increase in thermal contact with the crucible prevented complete melting of the sample. Since the vapor pressure of Mg at its melting temperature (650°C) is only about ∼3 mbar (Ref. [3]), the increase in pressure within the crucible is not sufficient to displace the molten ball of Ta (Fig. [h]), so that the crucible is successfully sealed. Assuming that the average temperature inside the crucible was about 600°C, the room-temperature Ar pressure inside the sealed crucible was approximately 1/3 bar.

The effectiveness of these crucibles was tested by a series of DTA measurements made in an attempt to determine solution-growth parameters for growing MgB$_2$, from a mixture of Mg and MgB$_2$. 9.7 mg Mg and 0.71 mg MgB$_2$ (which amounts to Mg$_{60.93}$B$_{0.07}$) were sealed in a crucible as described above, and subject to several DTA runs. The highest temperature reached was 1470°C, which lies outside of the calibration range of the instrument. The curve obtained from one of the runs after the sample had been at 1470°C, is displayed in Fig. 2. The sample was heated and cooled between 450 and 1200°C at a rate of 10°C/min. Upon heating, only one endothermic event, with an onset temperature of about 640°C, was observed, and upon cooling only one exothermic event was observed, also with an onset temperature of about 640°C. These results are consistent with the published Mg-B phase diagram, which shows no exposed liquidus for MgB$_2$ at ambient pressures, and a eutectic (essentially just the melting of pure Mg) at ∼650°C. Furthermore, the results indicated that solution-growth parameters cannot be determined in this way.

This experiment demonstrates quite clearly the good performance of the crucible. The sealed crucible allowed repeated heating cycles up to 1470°C, and its appearance did not change visibly due to the temperature cycles. The strength of the DTA signal due to the melting and solidification did not visibly change in any of the several runs that we performed, consistent with no Mg loss during the experiments. Note that at 1470°C, the partial pressure of Mg is about 12 bar and the Ar partial pressure is estimated at about 2 bar.

A second example demonstrates the usefulness of the sealed Ta DTA crucible for the determination of phase-diagram data. A total of 40.9 mg of Gd and Mg, corresponding to the composition Gd$_{40}$Mg$_{60}$, was sealed in a crucible, as described above. After alloying the elements by heating the crucible to above 1200°C, the DTA signals were recorded. The DTA results, measured upon heating

FIG. 2: Relevant part of the DTA curves of a sample of Mg and MgB$_2$ measured upon heating and cooling with a 10°C/min rate. The melting (and solidification) event near 640°C can clearly be distinguished.

FIG. 3: Relevant part of the DTA curves of a sample of Gd$_{40}$Mg$_{60}$ measured upon heating and cooling with a 10°C/min rate. The melting (and solidification) events near 750°C and 850°C can clearly be distinguished.
to 1100°C and cooling to below 400°C at 10°C/min are shown in Fig. In both curves, two events can clearly be observed. Upon heating, a sharp peak occurs at ~750°C, followed by an event typical of a liquidus event, ending near ~850°C. Upon cooling, an event, that is also typical of a liquidus, occurs with an onset temperature of ~840°C, followed by a sharp peak with an onset temperature of ~750°C. No further events were observed at lower temperature. These results are consistent with published phase diagram data, where the liquidus temperature for the composition Gd₄₀Mg₆₀ is reported near 850°C, below which the compound GdMg solidifies, followed by the (peritectic) formation of GdMg₂ at 755°C.

Both sealed and unsealed Ta crucibles fabricated as described above have been used routinely for DTA measurements in our laboratory for over one year. With experience, the failure rate in sealing the crucibles is minimal. Rare failures in sealing are easy to identify and discard and no successfully sealed crucible has failed during measurement, so that the instrumentation has not been exposed to reactive vapors. It should be noted that the use of Ta crucibles requires an extremely clean environment within the DTA, since Ta will oxidize rapidly and become brittle. The overall cost of the Ta crucibles is approximately the same as that of the commercially available ceramic crucibles.

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