Thermal Analysis sampling cups

by David Sparkman Oct 6, 2009 all rights reserved

Sampling cups are one of the consumables and can represent the major cost of thermal analysis. In this topic we will examine the different types of cups, the different results of each style and where they are most appropriately used, and the different kinds of problems each style has.

When sampling light metals, some systems will use a steel cup that has been coated with boron nitrate or other insulator. But with higher temperature metals such as iron, steel, nickel and other such metals, the steel cup is inadequate and is easily destroyed by the higher temperatures. The steel cup requires a sleeve for the reusable thermal couple and becomes the main "consumable" for this technique. This method is the most accurate method available as the cup is heated to the metal temperature and the temperature loss rate is only minimally affected by the cup. It is very easy to see thermal events at or above the liquidus with this technique. Phase diagram work has been done in light metals using this technique.

In almost other cases, a sand cup is used. The sand cup's benefits are: ability to be used with high temperature metals such as iron, steel, and nickel and cobalt based alloys. It is generally inexpensive, and can easily mass produced.

Sand Cups

The two largest suppliers of sand cups in the United States are ElectroNite and Minco. Both make adequate cups though they seem to have stopped any research and development on their products. Prices have risen on the tellurium based cups due to the increased demand for solar panels in the U.S.

There are a number of different versions of these cups: round and square tellurium cups for iron, round and square cups for iron C.E. or microstructure without tellurium, and cups for aluminum. I have problems with using sand cups for aluminum, it is very difficult to get a liquidus without superheating the aluminum and that picks up a lot gas. Sand cups for aluminum using the ceramic tube should NOT have a refractory coating. That coating further slows the temperature signal from reaching the thermal couple. It sometimes happens that a supplier will substitute iron cups for aluminum.

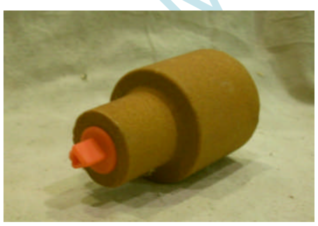
Here are the differences and what can go wrong:

ElectroNite Cups for iron: These cups are square based and will hold about 200 grams of iron. They feature a quartz enclosed butt welded thermal couple with the wiring running down the outsides of the cup. The cup comes in two versions: one for testing for C.E./Carbon/Silicon which contains about 5 grams of tellurium, some calcium bentonite, and some sodium silicate (water glass) mixed together to form a dark gray blob in the bottom of the cup, the second is for testing microstructure and is missing the tellurium blob. Strangely they often sell for the same price.

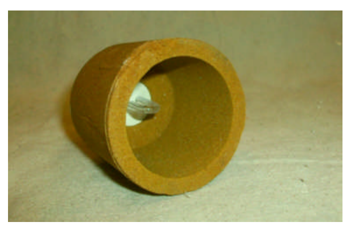
ElectroNite/L&N Cups for iron: These cups are round based and hold about 160 grams of iron. They feature a white ceramic tube in the middle of the cup and the two TC wires come up though the tube which ends with a few twists coated with a core wash. The tellurium is contained in the gray speckled wash inside the cup. This cup is a holdover from when Heraeus (parent of ElectroNite) purchased L&N Metallurgical Division, and then folded it into ElectroNite a few years later. Some customers did not want to change over to the square ElectroNite cup and insisted that ElectroNite continue selling this line. ElectroNite did continue the product, albeit at a higher price than the square cup. These cups are better at not failing with high sample temperatures because the core wash slows the heat getting to the thermal couple. Likewise these cups would not be as good with very low temperatures for the same reason. It should be noted that ElectroNite parent company is one of the world's largest supplier of quartz tubing.

Minco Cups for iron: These cups come in several different shapes and sizes imitating both the ElectroNite square cup and the older L&N style round cup. The bottoms come in both square and round styles. The round cups come in both 160 gram and 200 gram sizes. The tellurium used is a higher metallurgical grade and contained in a gelatin capsule glued in the bottom of the cup. The thermal couple is the ceramic tube kind in all styles of cups making it better for high temperatures and worse for extremely low temperatures.

ElectroNite Cups for Steel and high temperature metals: These cups are round and have a u shaped quartz tube in the bottom of the cup. The cup connector as well as the thermal couple is the same as is used in a temperature probe. The color of the plastic in the connector indicates the type of thermal couple with red indicating type 'S', and purple indicating type 'B'. Type 'S' is for temperatures up to 3028 degrees F, while type 'B' is good for up to 3308 degrees F. Type B uses 30% platinum and so is significantly more expensive.



Type 'S' Steel cup base



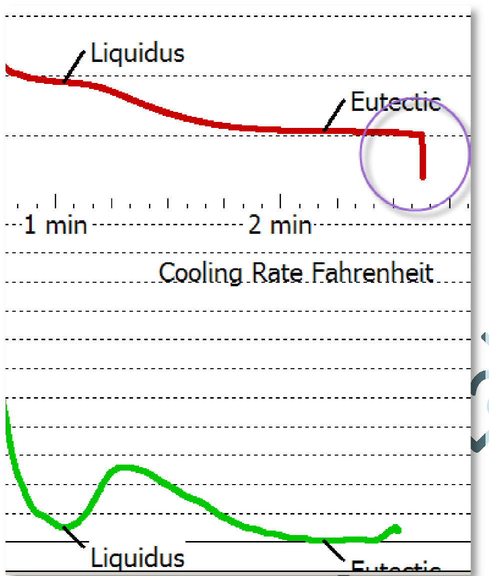
Steel cup thermal couple

Pros and Cons for tellurium Iron Cups – avoiding temp failure

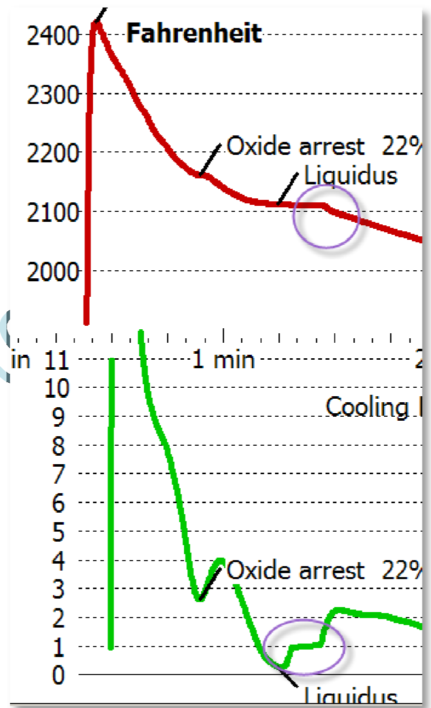
Each design has its strong points and its weak points. The quartz tube is better at analyzing lower temperature iron because the temperature reaches the thermal couple faster. But if the melting furnace temperature is on the high side, you will get fewer failures with the ceramic tube. The quartz tube type cup can fail in two ways.

First, the weld joint can soften and the weld pulls apart. MeltLab will show an immediate loss of signal, and, if you look at the cup, the wire will have sprung out about 3/16 inch on one side. Note, pulling the cup off of the stand will look the same as the signal is broken. Before assuming that you had a failure, consider that the operator might have removed the cup on purpose or that he may have unintentionally bumped the cup with the pouring spoon and broken the connection with the stand.

The second means of failure is when the quartz tube fails and molten metal gets inside the tube and touches the wire. MeltLab will show an almost instant drop of 10 to 20 degrees F in the curve and then continue as normal although at the lower temperature. This is due to current being bled off though th e contact with the molten metal (loss of electrical insulation).



Failure of TC Weld



Failure of TC insulation

These failures are generally caused by a poor weld or high sampling temperatures in the first case, or by a quartz tube that was bent and straightened in manufacturing thus thinning and weakening the wall of the tube. In the later case, this occurs if the thermal couple is manua lly manufactured, and doesn't if the manufacturing of the thermal couple is automated. Look at the top of a box of cups and you can notice any bending and straightening in the quartz tubes. Some manufacturing sites are automated and some aren't. From a quality standpoint, automation is great. Either you make a lot of bad products or you make very few from the same philosophy that it takes a computer to really screw up. With manual manufacturing, product quality can vary a lot.

The ceramic tube design can also fail though two means. First, if the ceramic wash over the tip of the thermal couple fails, the iron can get in and dissolve the nickel based thermal couple. This will produce an extreme drop in temperature and the MeltLab will terminate the analysis. The second type of failure is when the ceramic tube cracks under stress (or perhaps previously damaged in handling). The iron penetrates the crack and the temperature will rapidly drop 10 to 20 degrees then continue as if normal. Both of these failures appear similar to the weld failure and the insulation failure of the quartz tube style.

This is due to current being bled off though the contact with the molten metal. To understand this, consider that the actual current produced by the TC is less than 1 millionth of an amp, and that the top of the cup is discharging a small amount of electricity though static discharge to the roiling hot air over the molten iron.

Since the temperatures are artificially suppressed, any calculations based on temperature will be wrong. In the 1990's L&N experienced a great deal of trouble with this problem, and after the fact analysis pinpointed low density ceramic tubes as the cause. If you are using quartz tube type of cups look closely at the straightness of the tubes in a box of cups. Bent tubes or tubes with a kink in them have thinner walls and thus are weaker. This is especially problematic in the microstructure analysis of final ductile iron, where graphite growth exerts pressure on the mold walls and the quartz tube.

Pros and Cons for tellurium Iron Cups – tellurium failure

Tellurium prevents the formation of graphite. It does not prevent the growth of existing graphite. If undissolved graphite is present in the iron, the tellurium will not produce a true carbon/silicon analysis. Late additions of graphite, or using a graphite sampling spoon can throw off TA results. Tellurium becomes a vapor in the molten iron at 1814 degrees F (990 C), and reaches a maximum solubility of about 0.06% in the molten iron. This is sufficient to produce a white structure unless unreacted magnesium is present (MgO and MgS are examples of reacted magnesium). Minco cups come with a precisely controlled addition of tellurium (0.50 grams +/- 0.06g at 6 sigma), the ElectroNite method does not allow for that precise of a control of the amount of tellurium as it is a blended mixture of bentonite, water glass and tellurium. In the early days, the Minco pill would jump out of the cup, but Minco changed the glue and this is no longer a problem. The L&N process suspends the tellurium in a mixture of water, alcohol, and aluminum oxide core wash and then washes the mixture onto the cup.

The L&N method is the most difficult to control as there are 4 ingredients and the tellurium can easily settle out. The ElectroNite method has been fairly reliable due to the high viscosity of the bentonite. My concern is that with the doubling and quadrupling of the cost of tellurium, shortcuts could be taken. In the past, 0.5 grams was the standard for both Minco and ElectroNite. Actual requirements are 0.12 grams ***dissolved*** in the metal. Cheaper grades of tellurium are black due to oxidation. About 0.3 grams addition should be sufficient to achieve a dissolved level of 0.06 % as some of the tellurium escapes as a gas. Minco is best situated to accurately lower their addition. The ElectroNite method has to depend on a larger safety factor. Recalesence in the eutectic is the surest sign of insufficient tellurium if undissolved graphite and magnesium can be ruled out. The operator can also overfill the cup and dilute the tellurium causing a failure.

L&N sulfur cups/Magnesium testing cups

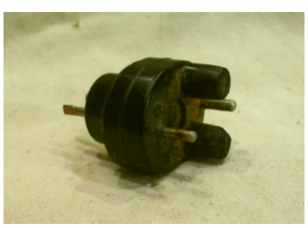
There is a technique pioneered by L&N to test for adequate magnesium in ductile iron by adding sulfur to a tellurium cup. The amount of sulfur in each cup is designed to neutralize a certain level of magnesium thus letting the tellurium cause a white structure. These are available designed to detect different levels of magnesium. Thus a cup designed for 0.030 magnesium will theoretically neutralize up to 0.03 % magnesium. If the cup then still shows graphite growth then the active magnesium is in excess of 0.03 %. If there is no graphite growth then the magnesium is insufficient or missing. This is a rough test because controlling the sulfur addition (using flowers of Sulfur) is not precise, (has iron sulfate been tried?) and the reaction of iron with the sulfur can change with fill rates. It excels in showing that the magnesium treatment did occur, but might not discriminate well with slightly undertreated iron.

Boiling and Bubbling tellurium

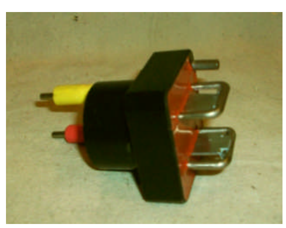
One ElectroNite publication actually said that the cup should boil for 5 seconds as if that were a good thing. It isn't. Moisture in the cups and especially in the water glass of the ElectroNite cups can cause excessive boiling in the sample. This makes the cup hard to fill to a consistent level, and lowers the carbon and silicon in the cup through the old green pole poling technique of yesteryear. Were these companies still trying to improve their product, they would quickly realize that there are ways to avoid boiling, and make better cups.

Cup connectors

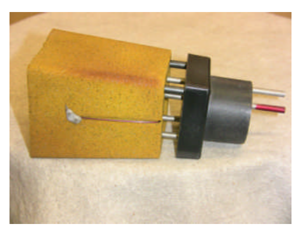
The round connector is traditionally made out of Bakelite, a poor connector substance. Bakelite turns conductive above 250 degrees F, and that changes the values of the thermal analysis curve. In addition, the connector easily breaks down with temperature and it becomes difficult to keep the cup from wobbling. I know of no good connectors for these round based cups. The market is very small and MeltLab Systems has chosen not to produce this style of cup connector for economic reasons.



ElectroNite Round bottom

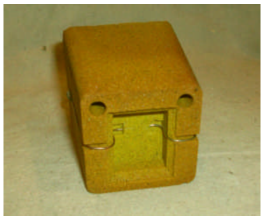


ElectroNite Square bottom



MeltLab square bottom

Round base



Square base

The square base connector has been made of all sorts of materials. Minco, after the death of the brilliant Bill Falk, made connectors out of nylon with such low melting points that they were instant failures. The connector needs to have greater than 10,000,000 ohms resistance between the rails, even when warmed by use. ElectroNite and MeltLab connectors achieve this. The MeltLab connector introduces a few innovations: 1) the cup is held up off the connector by 0.2 inches to slow down heat transfer to the connector, and 2) the alignment pins are higher to better support the cup up off the connector, and 3) the connector is made of Rytan 7, the material ElectroNite uses in its highest temperature steel mill products (but not in its iron products). This product did originally suffer some cracking from the alignment pin holes, but the problem has since been corrected.

The ElectroNite connector will generally fail when the red rubber begins to curl up and resin gets below the rubber where it cannot be removed though cleaning. Resin needs to be cleaned off between the rails with a wire brush to keep the rails insulated from each other. The rails also will become coated with resin and need to be cleaned for better contact. Generally a used cup can be used as an abrasive to clean the rails. Just rub the outside top corner of the rail with the sand cup fragment.

The square cup can be adjusted to loosen or firm up the cup sitting on it. Use channel lock pliers to either spread or to close up the distance between the rails until the cup sits firmly on the connector. Too much force putting the cup on can crack the cup. Pouring iron into a cracked cup will destroy the connector.

One last thing on cups and connectors: The red connector on K-type thermal couples is magnetic. Twice I have found connectors miss-colored. This resulted in the cup being detected, but going not-ready as soon as iron was added.

MeltLab high temp connector

P.S. for those interested, MeltLab high temperature cup stand connector P/N 2008X1 are $45 each or $40 each in quantities 5 and above.