The Los Angeles Silhouette Club

The Myth of Arsenic

By: Wiljen

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It has long been common knowledge that heat treat hardening ‘required’ arsenic to be effective. This is often demonstrated by showing that wheel weight alloy will harden after heat treating while linotype won’t. The term catalyst is often used wrongly to define the action of arsenic in hardening. In strict definition a catalyst is a substance that causes or accelerates a chemical reaction without itself being affected. Heat treat hardening is not a chemical reaction so the term is not appropriate. So if it isn’t a catalyst, what is it? To answer that, we first need to understand what is really going on in the process of “Heat treating”.

Heat treat hardening really isn’t the appropriate term either. What is actually happening is a process that has long been known as Hall-Petch Strengthening. Hall-Petch Strengthening is a method of strengthening materials by changing their average grain size. Typically, the smaller the grain size, the higher the strength exhibited. It is based on the observation that grain boundaries impede dislocation movement and that the number of dislocations within a grain have an effect on how easily dislocations can traverse grain boundaries and travel from grain to grain. So, by changing grain size one can influence dislocation movement and yield strength. As examples, heat treatment and changing the rate of solidification are ways to alter grain size.

If that last statement sounds familiar, it should, it covers the two most common methods of hardening cast bullets, namely heat treating and water dropping.

Many metals are altered using grain refiners to get the grain size down to 10nm as that produces the greatest strength. Grains larger than 10nm are subject to dislocation slip, grains smaller than 10nm are subject to grain boundary sliding. In the case of Pb-Sb alloys, arsenic acts as a grain refiner and allows us to reduce grain size and thus increase the strength of the alloy.

So there we have it, Arsenic is a grain refiner, not a catalyst.

Grain refiners are chemicals added to a molten metal or alloy to check grain growth and are found in many metallurgical processes. Titanium, carbon, and boron mixtures are commonly used as grain refiners in aluminum casting operations. Vanadium and niobium are commonly used grain refiners in steel manufacture. The most commonly used grain refiners have evolved over the years as improvements have been discovered. For example niobium is a better grain refiner in steel than is vanadium under most circumstances. Vanadium was the accepted norm for years, but is now being replaced by niobium in high stress applications as it yields greater strength.

So, if many different things can be used as grain refiners in aluminum and steel manufacture, why not Pb-Sb alloying. A quick study found that indeed several different materials are grain refiners for Pb-Sb alloys. Amongst these are Arsenic, Copper, Selenium, and Sulfur.

At this point, we can dispel another of the common misconceptions, arsenic is not required for heat treat hardening Pb-Sb alloys a grain refiner is, one of which is arsenic. Other grain refiners may be substituted for arsenic and may even produce a stronger alloy depending on conditions.

It is now time to leave our theoretical discussion, and start experimenting.

First I needed to find a source of each of the grain refiners. I talked to my local lead foundry and they agreed to make some test alloys. (More realistically, they agreed to keep samples of alloys produced for other customers that met my needs).

To test Copper, the alloy was a Babbitt material with 5% Tin, 6% Antimony, .5% Copper, and the remainder lead. This was mixed 1 part Babbitt to 2 parts lead to bring the Antimony concentration down to the standard 2% being tested in other alloys.

To test Selenium, the alloy was 2% Antimony, .25% Selenium, and the balance Lead. (This is an alloy commonly used in battery plates that the company had pre-made and readily available).

No alloy was available to test Sulfur so I produced one by using a base alloy made from 1 part linotype and 5 parts pure lead (both certified samples to avoid introducing unknowns) with a final composition of 97.3% Pb, .67%Sn, 2% Sb. To this Sulfur was added to the base alloy at a temperature of 900F and held there for a period of 1 hour to allow complete homogenization of the mix. The final sulfur concentration was .04%.

Finally, for our arsenic containing sample, the foundry produced an alloy as close to wheel weights as I could get. 2.2% Antimony, .5% Tin, .02% arsenic, and the balance lead.

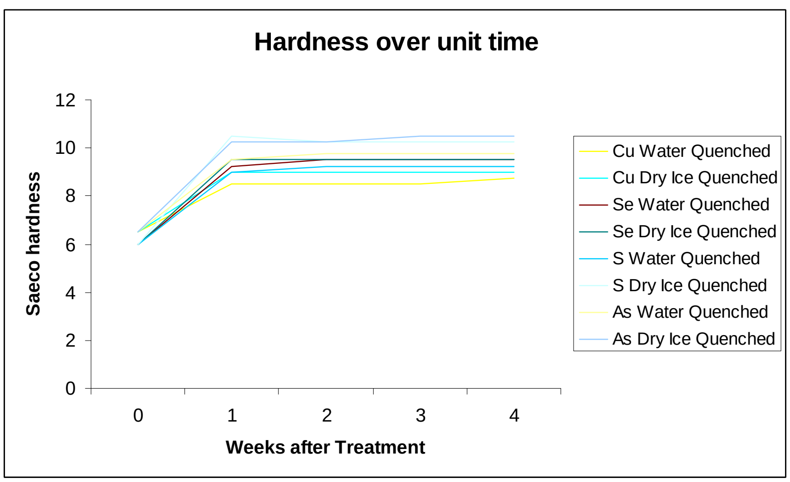
Due to the small sample sizes and my desire to run several different tests, I was going to have to be frugal with alloy. I decided to use the 358345 bullet because it was light and didn’t take much alloy and its large flat surface made for easy testing.

To keep from contaminating each batch, I did my casting using a cast iron pot over a turkey fryer and completely drained and sanded the inside of the pot with 400 grit emery cloth between batches to remove any residual.

The batches were marked on the bases and separated into groups, those to be used as control and those to be heat treated. Heat treating was done in 2 batches. The first batch was heated to 432ºF and held for 2 hours then dropped immediately into tap water (66ºF). The Second batch was treated at the same temperature for the same length of time but was dropped into a bath of Antifreeze (Peak pre mixed) and dry ice at a temp of (19ºF). Measurements were then taken at week intervals using a SAECO hardness tester on 4 of each type and the average taken. Care was taken not to use the same specimen twice so that a previous test would not invalidate the later runs.

Results:

Alloy	As Cast		Week 1		Week 2		Week 3		Week 4	
	Saeco	BHN	Saeco	BHN	Saeco	BHN	Saeco	BHN	Saeco	BHN
Cu untreated	6.5	10	6.5	10	6.5	10	6.5	10	6.5	10
Cu Water quenched	6.5	10	8.5	15	8.5	15	8.5	15	8.75	16
Cu Dry Ice quenched	6.5	10	9	17	9	17	9	17	9	17
Se untreated	6	9	6	9	6	9	6	9	6	9
Se Water quenched	6	9	9.25	19	9.5	20	9.5	20	9.5	20
Se Dry Ice quenched	6	9	9.5	20	9.5	20	9.5	20	9.5	20
S untreated	6	9	6	9	6	9	6.5	10	6.5	10
S Water quenched	6	9	9	17	9.25	18	9.25	18	9.25	18
S Dry Ice quenched	6	9	10.5	25	10.25	24	10.25	24	10.25	24
As untreated	6.5	10	6.5	10	6.5	10	6.5	10	8	11
As Water quenched	6.5	10	9.5	20	9.75	21	9.75	21	9.75	21
As Dry Ice quenched	6.5	10	10.25	24	10.25	24	10.5	25	10.5	25



As expected, all the grain refiners worked in the same way and with only mild variations in final strength regardless of the quenching method used. All showed similar patterns of the most significant gains being present by the end of one week with slight continued strengthening over the next 3. This is not atypical of other Hall-Petch strengthening results as dislocation will continue at a slow pace after hardening.

I hope this helps shed some light on arsenic and its role in casting. It may someday provide casters with alternatives as wheel weight alloy disappears and our sources of arsenic with it. All that is left now is to go shoot the test bullets and see if any differences in leading occur. I'll add the results of my shooting session when I get a chance to go to the range.

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