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Getting the Lead Out

Discarded electronics no longer pose an environmental hazard from lead solder thanks to a lead-free alternative developed at the Ames Laboratory.

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Lead has long been recognized as a highly toxic material that can cause brain damage. Its use in paint was banned in 1978, and it was later removed from gasoline to further protect human health. But a burgeoning source—electronic waste—posed a substantial new threat to the environment beginning in the 1990s as lead and other chemicals were leached from computers, computer monitors, televisions (with cathode ray screens), cell phones, and other electronic devices being buried in landfills. (Thankfully, flat screen monitors and televisions have replaced the lead-containing cathode ray screens in one "green technology" advance in recent years.)

Courtesy of Ames Laboratory

Figure 1. A wire (upper left) of Ames Lab lead-free solder, an alloy of tin, silver, and copper, is shown melting into a droplet at the end of a hot soldering iron (upper right).

The persistent source of lead in electronics was solder, the shiny metallic "glue" that holds components on circuit boards and bonds other electrical connections. Though a computer's circuit boards contain only small amounts of solder, the problem is overall volume. By some estimates, about 3,000 tons of electronic waste are discarded daily just in the United States.

To address the problem, Japan, the United States, and the European Union began moving in the early 1990s towards finding a replacement for common tin-lead electronic solder to limit the amount of lead and other hazardous materials lurking within the circuitry of all consumer electronics and industrial products. Thus in 1992 a team of researchers at the U.S. Department of Energy's Ames Laboratory focused their knowledge of materials science and metal alloy design and discovery on developing a lead-free solder, joining the others in the hunt. Given the global nature of the electronics industry, the eventual European ban of the product in July of 2006 was in essence international in scope. As electronics and appliance manufacturers scrambled to meet those tough new restrictions, many of them decided that the tin-silver-copper solder invented by the research team headed by Ames Laboratory was the most practical lead-free alternative (see Figure 1).

The challenge of replacing the lead in solder was tougher than it might sound. Traditional solder has been in use in some form for 5,000 years, and for electronic assembly it is a material with unusually good properties. Composed of lead and tin, solder melts instantly at one temperature (without turning "mushy" like solder for plumbing), flows easily, "wets" most conductors, and freezes quickly to create a strong, durable bond between the mating surfaces.

Traditional solder is an alloy, or a union of elemental metals. Moreover, it belongs to a special class of alloys known as "eutectic" (from the Greek word for "easily melted"). Eutectic alloys have the special property of melting at a lower temperature than the metals that compose them. They also act like a pure metal with a single melting (and solidification) point. A solder composed of 63 percent tin and 37 percent lead (by weight) behaves in exactly this fashion. In other words, its value as a binder is closely related to its eutectic properties.

Eutectic alloys also have a distinctive microstructure. When they freeze, the alloys form two distinct structures that are microscopically interspersed with each other in a characteristic manner that is readily identifiable with the use of a microscope. As the alloy melts, these interspersed structures disappear at precisely the same temperature to form a homogenous liquid.

The challenge, then, for the Ames researchers was to discover a new eutectic alloy that possessed the same functionality as the traditional tin-lead combination.

"Finding a substitute for lead to alloy with tin that gave the solder similar properties and melting behavior was difficult," says Ames Laboratory senior metallurgist Iver Anderson, team leader on the project. "We started from the tin-silver eutectic alloy that melted a little too high (221°C) for most electronic joining equipment and did not wet common conductors (like copper) well enough.

"Then we made the non-obvious choice of adding copper, which forms a higher eutectic with tin (227°C), to the tin-silver eutectic in an attempt to create a three element 'ternary' eutectic from tin, silver, and copper," Anderson continues. "The choice to add copper, instead of a lower melting element like bismuth, indium, antimony, or zinc, as many other researchers had tried, was based on the well-known 'curious' observation that silver and copper together form a relatively low melting eutectic."

In other words, instead of these very similar metals forming a continuous series of solid solutions, like copper and nickel, Anderson's team reasoned that they apparently have a strong interaction that favors a melting point depression that might help lower the melting point in a combined alloy with tin. In fact, the tin-silver-copper alloy in the composition region chosen by the researchers had been reported previously to display a higher melting reaction that occurred over a temperature range, i.e., mushy melting. However, the old report (1950) was based on a single data point in that composition region and no supporting semi-quantitative analysis with electron beam instruments.

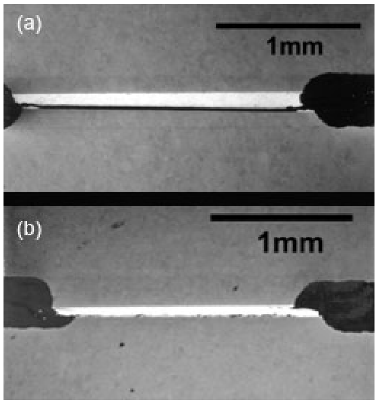
The Ames researchers prepared samples of several similar alloys, with compositions near to the datum from the earlier study, and then used a variety of instruments, including optical microscopy, wavelength dispersive spectrometry, x-ray diffraction analysis, and differential thermal analysis in their study. They established that while none of their first alloy choices was a ternary eutectic, the thermal analysis results and microstructures did show telltale signs that there was a nearby eutectic reaction. Based on sophisticated analysis of the structure and composition of that material, the researchers were able to then design a new alloy that was apparently what they had sought: a eutectic alloy that melted and froze precisely at one temperature. The researchers also subjected the new alloy to practical soldering trials to determine its utility as a substitute for the lead-containing product.

"Fortunately, our work resulted in the discovery of a lower melting (217°C) tin-silver-copper eutectic alloy that had sufficient levels of all of the desired properties, becoming an industry-preferred lead-free solder for many electronic circuit applications," Anderson says.

Anderson is environmentally conscious, due in part to his love of the outdoors and particularly from his nearly 50 years of alpine skiing near his hometown in Upper Michigan and while vacationing in the Rockies and elsewhere. He typically rides his bike to work at Ames and when he does drive, it's in his Prius hybrid. So helping keep the environment cleaner was a strong motivator behind the work, and the widespread use of his technology is a particular source of pride.

The Ames Laboratory's solder technology was patented in 1996 and has been licensed by nearly 60 companies worldwide. To date, those licenses have generated royalties in excess of $30 million. The Iowa State University Research Foundation (ISURF) holds the patents for research developed at Iowa State, including Ames Laboratory.

The Ames Lab solder is just one of several lead-free alternatives on the market. The type and specific composition of lead-free solder also depends on the soldering technique used and the end application. In addition to the tin-silver-copper alloy, Anderson's group developed modified alloys that also contain iron, cobalt and other similar elements. These blends, which have also been patented by ISURF, are suitable for higher-temperature applications, reducing the chance that solder joints will get brittle over time (see Figure 2a) after prolonged heating cycles. Heat has become a growing factor as technological advances in electronics (miniaturization and higher "clock" speeds) have boosted operating temperatures. For example, the steady climb in computer processor speeds has meant a corresponding increase in the amount of heat that processors generate.



Courtesy of Ames Laboratory

Figure 2. Optical micrographs of two solder joints (joining copper conductors, top and bottom) after thermal aging (1,000hr. at 150°C) and shear strength testing, where (a) is tin-3.6%silver-1.0%copper (wt.%) and(b) is tin-3.7%silver-0.6%copper-0.3%Zn, with the top conductor moved left and the bottom moved right on each sample.

"Even the circuitry in your cell phone operates at about 125 degrees Celsius," Anderson says, "and over six months' use, that can mean several hundred hours of high temperatures. If you drop it now, the solder joints have become more brittle and the risk of it 'breaking' is higher."

To further combat this solder "aging" problem, Anderson's group has recently been studying more additives to the tin-silver-copper formula, including silicon, titanium, chromium, manganese, nickel, zinc, aluminum, and germanium. Joints soldered with the different alloys were subjected to 150 C for 1,000 hours, and then tested for both shear strength (see Figure 2) and impact strength.

"Zinc appears to be most attractive in terms of retained ductility (see Figure 2b) and strength," Anderson says, "and also offers benefits in terms of solderability, ease of alloying, and material cost." While additional testing is needed, especially in an industrial environment, he adds that the tin-silver-copper-zinc composition can make a real improvement in joint reliability.

One other benefit of this recent work, funded by the Laboratory's royalty revenue and industrial partners, is development of a simple and fast technique for characterizing the bulk composition of solder joints using wavelength dispersive spectroscopy. This permits Anderson's research team to analyze the new compositions being studied under different soldering conditions.

"With the elimination of lead, tin-silver-copper solders are here for the long run," Anderson says. "But that doesn't mean we'll stop trying to improve our basic understanding of how these alloys work during and immediately after soldering and after many hours, days, or years of use in order to improve their performance."

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Publication

C. M. Miller, I. E. Anderson and J, F. Smith, "A Viable Tin-Lead Solder Substitute: Sn-Ag-Cu," *J. Electronic Mater.* **23** 595 (1994)

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