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Lead-Free Copper Alloy Development

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ABSTRACT

Copper alloys containing lead (Pb) as an alloying element were regularly used for drinking water applications. In response to the call to reduce the lead content in drinking water, the industry has introduced many lead-free alloys since including the bismuth-containing alloys developed in the AFS led consortium in 1990's. Since then, these alloys have evolved and replaced lead-containing copper alloys in drinking water applications all over the world. Industry has adopted new processing technologies and testing methods to make the lead-free alloys widely usable in an affordable way. This paper reviews these developments in bismuth-containing and other lead-free copper alloys since the early announcements.

Keywords: copper alloys, lead-free, castings, plumbing, corrosion testing, drinking water

INTRODUCTION

Copper and its alloys have been used for drinking water applications including pipes, valves and faucets since the early 1900s. The excellent corrosion resistance of these alloys in drinking water is the major reason for the extended use. Copper alloys develop passive surface layers when exposed to drinking water. This coating moderates the corrosion rate as well as reduces the leaching of metals into the drinking water.

Plumbing components have traditionally been made from sand cast red and semi-red brasses (alloys C83600 and C84400) containing lead as one of the alloying elements. The lead content of these alloys varies between four and eight percent. Lead, in brasses, provides two advantages: pressure tightness and ease of machining. Lead is insoluble in solid copper and found as finely distributed globules in the inter-dendritic areas of the cast alloys contributing to the pressure tightness and machinability.

However, the findings that lead can cause developmental challenges, especially in children, made governments introduce regulations controlling lead content in drinking water. Leaded-copper alloys used for plumbing applications, including solders and components, were identified as possible sources of lead.

The Lead and Copper Rule (LCR) is a U.S. Environmental Protection Agency (EPA) regulation that allows a maximum 15 µg/L (15 ppb) of lead in potable water. Other jurisdictions including EU and Canada proposed limits to 5 µg/L (5 ppb). In conjunction with the Lead and Copper Rule, the EPA commissioned National Sanitation Foundation International (NSF) to develop standards for measuring, approving, and monitoring lead, copper, and many other metals and chemicals that can be introduced into potable water. In response to this, NSF has developed several standards addressing these requirements, most notably NSF Standard 61. The NSF has also established the lead action limit for point-of-use products (faucets) and in-line mechanical devices at 11 ppb. This is lower than the EPA's 15 ppb or 15 µg/L limit because the EPA assumes that the additional 4 ppb could be contributed by other sources.

Apart from this limit, the Safe Drinking Water Act (SDWA) by the US EPA has reduced the maximum allowable lead content—that is, content that is considered "lead-free"—to be a weighted average of 0.25 percent calculated across the wetted surfaces of pipes, pipe fittings, plumbing fittings, and fixtures and 0.2 percent for solder and flux. While it is possible to surface treat the lead-containing copper alloys to reduce the lead intake by drinking water, the limits on allowable lead in alloys necessitate the development of lead-free copper alloys and solders with less than 0.2% Pb. Because of the presence of lead in brass scrap, none of the secondary casting alloys are truly lead-free. Thus, although no lead is intentionally added, a small but measurable amount of lead is typically present in many copper casting alloys.

Early on, lead-free solders were introduced for drinking water applications and the trend is continuing for solders used in other industrial applications. Attention was later focused on components such as valves and faucets which led to the development of various low-lead alloys to replace leaded-copper alloys.

LEAD-FREE ALLOYS

Many new copper alloys were introduced in response to the requirement of low lead content since the early 1990s. The common alloying additions were bismuth, selenium, silicon and sulfur. The developments along with processing, machinability and corrosion behavior of these alloy systems are briefly discussed as follows.

BISMUTH-CONTAINING ALLOYS

Bismuth is insoluble in copper and segregates to grain boundaries very similar to lead. But instead of staying as globules similar to lead, bismuth remains as a film along the grain boundaries in pure copper. This makes the material brittle and bismuth in pure copper and some other alloys restricted to less than a few hundred ppm. However, it is possible to reduce the wettability of bismuth by alloying. This makes the bismuth solidify as globules in inter-dendritic regions and can contribute to ease of machinability. Most common elements that can help include tin, lead, zinc and antimony.

The earliest low-lead alloy was patented in the 1970s in the UK.[1] Selenium was found to make a synergistic contribution to the machinability of bismuth copper alloys.[2] Extensive research and development work supported by a consortium led by the American Foundry Society (AFS) and conducted at CANMET Materials Technology Laboratory (MTL) [3,4] resulted in the development of three alloys known as EnviroBrass.

- EnviroBrass I (C89510), and EnviroBrass II (C89520) were developed as substitutes for C83600 leaded red brass and C84400 semi-red brass.
- EnviroBrass III (C89540) is a substitute for C85800 leaded yellow brass.

During the same period, research efforts had identified mischmetal as a possible additive along with bismuth to improve machinability. The first U.S. Patent #5,487,867 was granted in 1996 which covered the addition of 0.1 to 7% bismuth and 0.1 to 2% mischmetal to replace lead in copper alloys. A family of four alloys, known as FederAlloys®, were introduced to replace red brasses (C83600, C84400) and tin bronzes (C92200, and C93300).[5] The four new alloys were later listed by the Copper Development Association (CDA) and the American Society for Testing and Materials (ASTM) without mischmetal requirements.

As the cost of selenium increased manyfold due to the demand in other industrial applications in early 2000 selenium was removed from EnviroBrass alloys and new lead-free alloys with bismuth were introduced. Research efforts funded by the Brass and Bronze Ingot Manufacturers, AFS and copper foundries led to the development of bismuth-containing alloy C89836.[6]

The alloys containing bismuth melt at marginally higher temperatures of 1030C (1885F), due to the higher copper content. The freezing range is 170C (300F), very similar to those of red brasses. Hence, to achieve similar superheats used for red brasses the pouring temperatures need to be marginally higher. Conventional gating and feeding systems employed for lead-containing alloys could be successfully used for bismuth-containing alloys. Bismuth-containing alloys reported to have better resistance to hot tearing than the leaded alloys.[7]

While the focus in North America was on sand cast lead-free alloys, efforts in Europe and Asia were on high zinc alloys for use in permanent mold casting. High zinc alloys having up to 40% Zn were tested with various levels of bismuth. EnviroBrass 3 is a high zinc alloy with bismuth and selenium replacing 2% lead.[4]

SILICON-CONTAINING ALLOYS

There are several other possible copper-based alloys with low lead contents and good machinability. These include silicon brasses and bronzes, which can offer excellent casting characteristics in sand and permanent molding operations.

Sambo of Japan introduced a Cu-Si alloy containing phosphorus and zirconium as alloying elements with the trade name ECOBRASS.®[8,9] The fine grain structure is the major reason cited for the ease of machinability. Zirconium can be used as a grain refiner in red and silicon brasses. Originally introduced as wrought alloy, this alloy has two variations for sand and permanent mold casting and has the CDA designation C87850. The alloy listed in CDA does not mention zirconium.

The Cu-Si alloys melts at significantly lower temperatures than red brasses and can be cast in both sand and permanent molds. The liquidus of the alloy is 890C (1635F) and has a freezing range of 50C (80F).

SULFUR-CONTAINING ALLOYS

Sulfur in copper alloys is considered an impurity and always kept very low. Sulfur in the presence of oxygen may cause SO_2 formation on melting and result in gas porosity during solidification. Sulfur also forms sulfides with copper, zinc and manganese present in copper alloys. In pure Cu-S alloys these sulfides are Cu_2S which can be observed in grain boundaries and interdendritic areas. In the presence of other alloying elements, the sulfides are observed to be complex structures.[10] New copper-tin-zinc alloys are being introduced using sulfide particles as the source of improved machinability.

A new alloy, commercially known as Biwalite,® is registered as Unified Numbering System (UNS) alloy C83470 and can be used as a lead-free alternate for plumbing applications.[11] The alloy has a sulfur content between 0.2% and 0.6% which is present as a compounded sulfide of copper and zinc. The volume of particles increases with the sulfur and zinc content. The sulfides are observed as eutectoid in the inter-dendritic areas and are the major source of machinability. Sulfide particles also have influence mechanical properties and properties are significantly affected beyond 0.7% sulfur.

The nature of the compounded sulfide changes with an increase in zinc content. It has been reported that a higher percentage of zinc will result in an increased amount of ZnS which is harder than Cu_2S. This significantly influences machinability. The optimum zinc content is reported to be less than 4%. Tin and nickel do not have much effect on properties.[12,13]

The melting behavior of Cu-S alloy is reported to be like tin bronzes. During the casting operation, it must be superheated to 1220C and poured at 1150C. The alloy is deoxidized with phosphorus by adding Cu-P before pouring as like other copper alloys.[14]

MACHINABILITY

Machinability is one of two major factors to be considered when lead-free copper alloys are introduced. The plumbing components undergo extensive machining before going into service and any changes or difficulties in machining will make the production of components expensive. Machinability is assessed using various factors including ease of cutting (energy and time), tool life, surface quality, chip form, and cutting force. In general, the performance of free-cutting brass, alloy C36000, is taken as standard and assigned a ranking of 100. Based on the performance, alloys are ranked as free-machining (70-100%), readily machinable (30-70%) and difficult-to-machine (rating less than 30%).

The bismuth-containing new lead-free alloys have machining characteristics similar to leaded brasses but require machining fluids for optimum machining performance. Even though bismuth-containing alloys possess similar physical and mechanical properties compared to leaded alloys, they suffer from low ductility and care should be exercised while machining these alloys to minimize the potential for cracking during machining operation. It may be possible that the loads applied during un-lubricated machining are too high for these alloys. Moderate loading and some lubrication may mitigate this problem.[15]

The machinability of sulfur-bearing alloys is found to be similar and marginally better than the free-machining brass. The sulfide particles are found to contribute to the ease of machining.

CORROSION

Copper and its alloys are widely known for their corrosion resistance to water. It is necessary to confirm the new lead-free alloys undergo similar interaction with drinking water. Many studies were conducted on lead-free copper alloys comparing their performance with conventional alloys. Weight loss, potentiodynamic polarization and long-term immersion tests were used. Dezincification resistance of the high zinc-containing alloys was also evaluated.[6, 16]

Initially the corrosion behavior of the lead-free alloys C89520 and C89530 (EnviroBrasses) had been evaluated and compared to conventional lead-containing alloys. These new alloys had marginally higher copper content and were similar or marginally better resistant to corrosion. Subsequently the selenium-free alloy C89836 was evaluated using weight loss, linear and potentiodynamic polarization measurement methods and was compared to that of C89520 (EnviroBrass II). The weight loss data indicates that alloy C89836 is marginally better than alloy C89520. The trend is not very clear when corrosion potential data is considered. So, it can be concluded that both alloys will perform similarly.[6]

The “Water Service Line Fittings Committee” under the American Water Works Association (AWWA) is responsible for AWWA C800 Standard for Underground Service Line Valves and Fittings.[17] The committee reviewed the literature to understand the current state of knowledge on the corrosion of copper alloys used in underground installations for drinking water. This review included the effect of soil which is present around the underground waterlines and fittings. This study indicated that there are no common testing procedures that are suitable for all alloys. Also, it is necessary to develop long term corrosion data for the alloy systems to provide guidance for future alloy development and applications. It proposed a group of experiments which could be used.[18]

SUMMARY

The copper alloy industry has introduced many new lead-free alloys for drinking water applications to mitigate the health implications of lead present in drinking water. The industry had to adopt new manufacturing techniques and develop test methods to implement these new alloys for wider acceptance. These alloys will serve humankind for many more centuries as copper alloys before for more than six millennia.

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