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A COMPARISON OF LEAD-FREE[1] COPPER ALLOYS

Introduction

For nearly two decades, NIBCO has been at the forefront of development and commercialization of lead-free potable water plumbing alloys. In fact in 1993, NIBCO was the first manufacturer to introduce a "lead-free" brass into the domestic plumbing market. This alloy, listed in ASTM B584 as Copper Alloy C89844, was the forerunner of the current family of copper bismuth alloys that includes both Copper Bismuth Alloys C89833 and C89836.
(See Table 1 for Alloy Compositions).

More recently, NIBCO launched a complete product offering of valves and fittings that are in compliance with recent national lead-free legislation. Rather than settling on a copper bismuth alloy, NIBCO has focused the recent lead-free launch on copper silicon alloys; including Copper Alloys C87850, C87600 and C69300. NIBCO elected not to just reintroduce a version of the copper bismuth alloys due to experience with the alloys, including more than a decade of continuous investigation, testing and research.

This paper explains the reasoning behind the evolution of NIBCO® lead-free products away from bismuth brasses. It mentions only in passing other lead-free alloys that will be addressed fully in subsequent NIBCO Technical Bulletins and Engineering Data Sheets.

TABLE 1

COPPER PLUMBING ALLOYS — NOMINAL CHEMICAL COMPOSITIONS (%)

Cast Leaded Copper Alloy	Copper	Tin	Lead	Zinc	Silicon	Bismuth	Phosphorus	Selenium
C84400	81	3	7	9	—	—	—	—
C83600	85	5	5	5	—	—	—	—
C92200	88	6	1.5	4.5	—	—	—	—

CAST BISMUTH COPPER ALLOY

Cast Alloy	Copper	Tin	Lead	Zinc	Silicon	Bismuth	Phosphorus	Selenium
C89520	86.5	4.7	—	8	—	1.5	—	0.2
C89844	84.5	4	—	8	—	3	—	—
C89836	89	5.5	—	3	—	2.5	—	—

WROUGHT BISMUTH COPPER ALLOY

Alloy	Copper	Tin	Lead	Zinc	Silicon	Bismuth	Phosphorus	Selenium
C49300	60	1.5	—	36	—	1.2	—	—

CAST SILICON COPPER ALLOYS

Alloy	Copper	Tin	Lead	Zinc	Silicon	Bismuth	Phosphorus	Selenium
C87600	89	—	—	5.5	4.5	—	—	—
C87850	76	—	—	20.9	3	—	0.12	—

WROUGHT SILICON COPPER ALLOY

Alloy	Copper	Tin	Lead	Zinc	Silicon	Bismuth	Phosphorus	Selenium
C69300	75	—	—	21.9	3	—	0.10	—

[1] Lead Free refers to the wetted surface of pipe, fittings and fixtures in potable water systems that have a weighted average lead content ≤ 0.25% per the Safe Drinking Water Act (Sec. 1417) amended 1-4-2011 and other equivalent state regulations.

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Bismuth and Silicon - Properties, Characteristics and Other Considerations

A discussion of bismuth copper alloys and silicon copper alloys needs to start with the elements themselves. The following examination of bismuth and silicon should provide the foundation for a better understanding of each alloy group.

Health Effects

NIBCO has always held to a basic tenet that any replacement of lead in plumbing alloys should not bring about health concerns. Just as the levels of lead in drinking water may be regulated in some jurisdictions, other constituents may leach from lead-free plumbing alloys. Such other materials and/or their use may be regulated as well. Bismuth may not be considered in the category as lead in terms of research regarding potential health hazards; however, since NIBCO first began researching alternative alloys for manufacturing in the early 1990s, the element of bismuth has received some scrutiny with respect to research regarding potential leaching and possible effects on human health.

First, it should be noted that *Silicon* is not a regulated substance and there is no published information indicating that Silicon may pose drinking water health risks.

In contrast, NSF published action levels for products containing *Bismuth* on August 2, 1995. This NSF notice was issued three (3) years after NIBCO's initial offering of the C89844 alloy when there was very little production of the alloy in the flow control industry. For bismuth, NSF/ANSI 61 – 2009 had listed the Single Product Allowable Concentration (SPAC) at 0.010 mg/l for Non-Section 9 articles and 0.050 mg/l for those covered by Section 9.

For reference, *Lead* has an NSF SPAC of 0.0015 mg/l and *Copper* has an SPAC of 0.13 .

It should be further recognized that some high zinc plumbing alloys contain *Arsenic* as an inhibitor against dezincification corrosion. Arsenic has an SPAC of 0.001 mg/l, as issued by NSF in October 2001. Again, arsenic is regulated but does not necessarily migrate appreciably from these alloys into potable water.

Source and Availability

The USA has no bismuth deposits. China, Mexico and Peru are leading producers of bismuth with China accounting for 40% of world production. Bismuth is only about twice as abundant as gold and is extracted from the earth's crust primarily as a by-product of lead mining. Domestically, recycling accounts for approximately 15% of bismuth production.

Silicon is the second most abundant element (25.7%) within the Earth's crust, second only to oxygen.

Melting Temperature

The melting temperature of bismuth is 520.7° F, which is significantly lower than the melt point for lead, 621.5° F.

Elemental silicon melts at 2572° F. The melting point of silicon is not a factor with respect to alloy application and service.

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[3] See Table e1 - NSF Drinking Water Criteria (not externally peer reviewed).

[4] *See* U.S. Environmental Protection Agency and Health Canada - NSF/ANSI 61

Alloy Solid Solubility

Bismuth and lead have relatively low solid solubility in copper alloys. As such, during casting, these elements solidify into low-melt point pools throughout the alloy matrix, filling porosity voids and providing advantages for chip breaking during machining.

Silicon has a high solid solubility within copper alloys, and as such, provides no benefit with respect to filling porosity voids. However, silicon in combination with phosphorus enhances alloy machining and improves corrosion resistance.

Basic Physical Properties

Bismuth is very brittle in contrast to lead which is extremely ductile. Also, neither of these elements adds strength to the copper alloys.

Silicon acts to strengthen copper alloys. (See Table 2).

Physical and Chemical Characteristics

Elemental bismuth is one of a very few substances that is denser as a liquid than as a solid. (Water is another well-known substance with this rare characteristic.) Bismuth expands when it freezes.

The melting point of silicon is much too high to be of any consequence with respect to physical or chemical characteristics.

Silicon does improve corrosion resistance of copper alloys, creating a largely impenetrable surface oxide barrier to corrosion attack. This surface barrier can be effectively removed prior to soldering through sound cleaning practices. (See NIBCO Technical Bulletin, NTB-0910). The protective surface barrier also provides a useful witness to over-heating during soldering. The surface of a silicon copper alloy turns a distinguishable brown color when it is over-heated, indicating a poor solder joint may have been made. If a poor quality joint is suspected, the plumbing component can be removed (sweated) from the water line and after proper preparation, it can be soldered back into the line without damaging the component.

Non-Technical Considerations

Bismuth migration from plumbing components into drinking water was not an issue in 1993 when NIBCO first introduced the C89844 bismuth copper alloy to the domestic marketplace. However, in the intervening years, NSF issued an action level for bismuth. Although NIBCO does not expect there to be an issue with levels of bismuth in drinking water, the fact that an action level was set by NSF prompted NIBCO to take a closer look at whether a bismuth-based product offering may be the best option for NIBCO customers. NIBCO chose to be proactive in considering the possibility that the use of bismuth in plumbing products may be regulated and/or permissible contaminate levels reduced with regard to the alloy in the future in relation to drinking water.

The Rationale for the Switch to Silicon Copper Alloys

Technical Considerations

Mechanical Properties at Room and Elevated Temperatures

Mechanical strength was an important consideration for NIBCO in weighing the advantages and the disadvantages of various lead-free alloy options. Our research and the elemental properties of the silicon copper family of alloys support that the strength of such alloys, including C87600, is far superior to bismuth copper alloys. (See Table 2).

TABLE 2
ROOM TEMPERATURE — MECHANICAL PROPERTIES COMPARISON

Alloys	Ultimate Tensile Strength (psi)	Yield Strength (psi)	% Elongation
Leaded Copper Alloy C83600	30,000	14,000	20
Bismuth Copper Alloy C89836	33,000	15,000	20
Silicon Copper Alloy C87600	66,000	32,000	20
Silicon Copper Alloy C87850	59,000	22,000	16

Further consideration was given by NIBCO to mechanical properties of alloys at elevated temperatures. Plumbing components can see exposure to high temperatures during manufacturing, installation and while in service.

As noted above, bismuth is identical to lead as far as being distributed throughout the copper alloy in the form of small pools, filling voids and improving machining. Second, the melting temperature of bismuth is 100° F less than Lead. Third, the inherent expansion characteristic that bismuth displays as it cools from a liquid to a solid is not seen as an advantage for a constituent within the alloy.

As early as 1992 NIBCO analyzed how the bismuth particles trapped within the alloy respond to high temperatures. More importantly, NIBCO considered how the mechanical strength of the alloy may be impacted by such exposure.

NIBCO considered these questions before its initial C89844 alloy launch in 1993 and recommended that temperature limits be placed on bismuth copper alloys.

NIBCO conducted elevated temperature tensile testing, which revealed that mechanical properties, Ultimate Strength (UTS), Yield Strength (YS) and Ductility, measured by % Elongation, decreased significantly as exposure temperatures increased beyond 200° F. NIBCO found further that:

- The strength of alloy C89844 decreases significantly at elevated test temperatures;
- At 250° F, C89844 strength values dropped more than 50% from room temperature values;
- Ductility was reduced nearly 90% at 250° F compared to room temperature; and
- The performance of alloy C89844 was not expected to be exceptional when compared to other bismuth copper alloys.

These findings were later confirmed independently in a study conducted by CANMET – Materials Technology Laboratory[5]. This study focused on the C89836 bismuth copper alloy.

In contrast, the silicon copper alloys C87600, C87850 & C69300 maintain good mechanical strength well beyond the levels of the bismuth copper alloys.

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[5] *See* High Temperature Strength of Cu Alloy C89836; M. Sadayappan, J.P. Thomson and M. Sahoo; CANMET – Material Technology Laboratory, Natural Resources Canada.

NIBCO considered the relevance of the high temperature property issues with regard to bismuth copper alloys in real world flow control applications and found the following:

1.) Bismuth copper alloys require specific care, including flood cooling, when they are machined so as not too locally overheat the work-piece. Such excess heating can cause cracking that can often not be detected until later in the manufacturing process.

2.) Care must be taken when soldering bismuth copper alloys during assembly and in service to ensure external forces are not applied to the parts while still in a hot condition.

3.) During soldering, there is no visible witness of over-heating of the component as is found with the surface discoloration of silicon copper alloys during soldering. Thus, it is not possible to determine from looking at a bismuth copper alloy part during soldering whether it had been over-heated and potentially damaged.

4.) Conservative and often unacceptable limits on service temperatures appear to be the only way to truly ensure that bismuth copper alloys can be safely used in flow control products.

A Place for Bismuth Alloys

It should be noted that NIBCO still recognizes there is a place for bismuth plumbing alloys in the market place. Clearly, certain plumbing applications do not require the use of an alloy with high temperature performance, leaving bismuth alloys as a viable option in these situations. Also, many of the mechanical property short-comings of these alloys can be compensated for through design modifications, such as by increasing product weight and wall thickness.

NIBCO weighed the limitations of the bismuth alloys against the product requirements of and expectations for NIBCO products and concluded the best fit was an upgrade to the silicon alloys. This is in line with the NIBCO tradition of being in the forefront of development and innovation.

Conclusion

A mounting body of evidence led NIBCO to the selection of silicon copper alloys for this second launch of improved NIBCO® lead-free products instead of continuing down the development path of bismuth copper alloys. This evidence was both practical and technical in nature and covered most aspects of new products, including safety and basic functioning. For the reasons outlined above, NIBCO has chosen silicon copper alloys for use in its lead-free product offering and believes such alloys to be the best choice in providing safe and quality lead-free product alternatives to the market place.

About the Author:

Ben Lawrence, a degreed metallurgical engineer for NIBCO INC., has nearly 30 years of experience in metals manufacturing, application and testing. He has contributed to NIBCO over the past 20 years in various positions, including corporate metallurgist and R&D manager. He is a member of AFS and has participated in CDA and ASTM standards development. Due to his extensive knowledge and experience, he is regularly consulted by plant and field engineers, as well as having played a role in furthering the development of “lead-free” alloys. Mr. Lawrence holds a bachelor’s degree in metallurgical engineering from Western Michigan University in Kalamazoo, Michigan.