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Spontaneous room temperature extrusion of Pb nano-whiskers from leaded brass surfaces

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We report that lightly abrading the surface of a commercial leaded brass results in the room temperature spontaneous growth of Pb whiskers and hillocks. The aspect ratios and submicron diameters of the whiskers that form render them easily dispersible in the atmosphere, with potentially serious health effects, especially for people that deal with leaded brass on a daily basis.

Brasses, Cu–Zn alloys, are extensively used both in industry and in consumer products. Lead (Pb), usually with 1–2 wt%, is added to some brasses to improve their machinability[1] and/or corrosion resistance.[2] Because of its good machinability, electrical and thermal conductivity, corrosion resistance, and mechanical properties leaded brass is widely used in electronic equipment, construction, plumbing, and common mechanical parts, such as gears and watch or clock parts. The supply of brass mill products in the United States reached 1.4 million tons in 2003, followed by 1.1 millions tons both in Japan and in Germany.[3] Whereas the annual brass supply in the United States increased by 1.3 times in the past 20 years, the Pb used in brass (≈15,000 tons) increased by more than 5 times.[3] This is an indication of the increased use of leaded brass—the industry standard for "free-machining" copper alloys[1]—in the brass family.

Lead is one of the oldest known and most widely studied occupational and environmental toxins and its harmful effects on human health[4–12] have long been a concern. For example, the leaching of Pb into potable water is a problem that is currently being addressed at least in the U.S. and Europe.[13] Most relevant to this work, biological and environmental monitoring has shown that Pb exposure levels were high in three brass and bronze industries, in which the highest Pb levels were observed in a foundry where a scrap grinding operation was performed and the Pb limits were exceeded.[6] Interestingly, the environmental concentrations and levels of other metals in that same study were within reasonable limits.

The room temperature spontaneous growth of Pb whiskers from commercial leaded brass was discovered by accident, when a leaded brass, with a Cu–38Zn–2Pb composition (ASTM-C37700) was used as a support for another experiment. The brass in question was machined into small cylinders and exposed to the atmosphere for an unknown time, but no less than a year. Prior to its insertion in a field emission scanning electron microscope (SEM) equipped with an energy dispersive spectrum (EDS) analyzer, the surface was abraded lightly with silicon carbide paper (FEPA P#800) to remove the native oxide layer and cleaned with acetone.

Roughly 2 h after the sample was abraded, whiskers—which EDS analysis confirmed to be comprised of pure Pb—of various morphologies were observed to grow from the brass surface (Fig. 1). In one area a hillock at the root of a long curved whisker was observed (top right in Fig. 1). The whisker diameters ranged from 20 to 500 nm and their lengths from a few to tens of microns. SEM micrographs taken 8 min apart (Fig. 2) confirmed that the whiskers grew, like hair, from their base. The axial striations suggest that the whiskers were extruded from the

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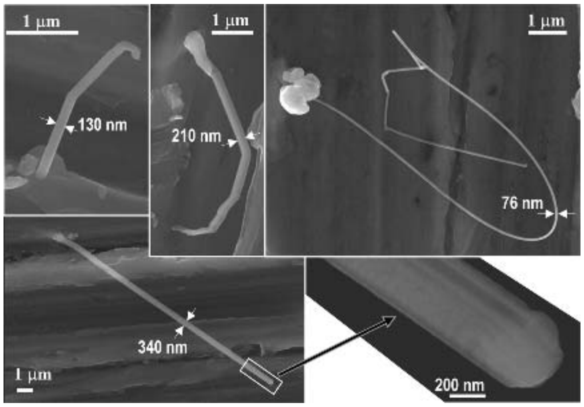

FIG. 1. Collection of Pb whiskers observed on the surface of a commercial leaded brass surface about 2 h after being lightly abraded with sandpaper. Striation in both the longitudinal and transverse directions are observed as shown in inset. The diameters of the whiskers ranged from a few tens to a few hundreds of nanometers. In the top right micrograph, a Pb hillock at the root of a curved thin Pb whisker was also observed.

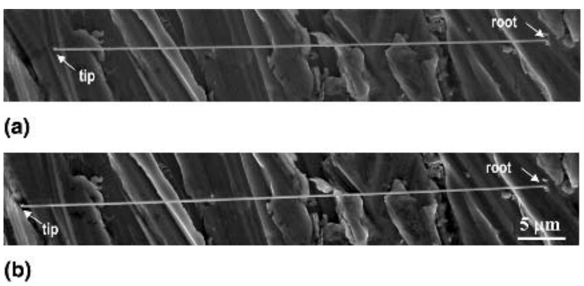

FIG. 2. Pb whisker growing from the surface of a commercial leaded brass surface (a) about 200 min after the surface was abraded and (b) 8 min later. In that short time, the whisker grew by about 3500 nm for an average growth rate in that time of 7.3 nm/s.

substrate. Striations perpendicular to the whisker axis were also seen, which may indicate the extrusion was not continuous, but occurs in tiny spurts. To establish the composition of the whiskers without interference from the substrate, some of them were transferred to a conductive carbon tape; in the process of transferring them, many broke into multiple smaller segments.

The whisker shown in Fig. 2(a) was observed about 200 min after the surface was abraded. If one assumes the growth was uniform and started immediately upon abrasion, this translates into an average growth rate of 4.5 nm/s. When the same whisker was observed 8 min later however, its length had increased by 3500 nm for an average growth rate of 73 Å/s. If one further assumes that the growth is along the close-packed $\langle 111 \rangle$ direction, such a growth rate corresponds to 26 atomic layers per second. Forty five minutes after the micrograph shown in Fig. 2(b) was taken, the whisker had not changed in length, implying that the whiskers grow in an intermittent manner. Note also that the growth spurt caused the whisker to rotate slightly counterclockwise [compare Figs. 2(a) and 2(b)].

The spontaneous room-temperature growth of low melting point or soft metal whiskers, such as Sn, Cd, Bi, and Zn,[14–17] as well as Al at elevated temperatures,[18] is a well-established phenomenon that had resisted interpretation for over 50 years. Quite recently, however, an oxidation-based model was proposed to explain this phenomenon.[19] In that paper, it was postulated that the volume expansion associated with the diffusion of oxygen down the grain boundaries of the soft metal is the driving force responsible for the extrusion of the latter. The results of this work not only confirm the basic tenets of this model, but also shed more light on the process. In the model, it was argued that rate at which the oxygen was diffusing into the matrix had to be decoupled from the whisker growth rates because in many cases the latter were much faster than can ever be accounted for by the instantaneous or concomitant oxygen diffusion. The very rapid whisker extrusion observed herein, 73 Å/s, is evidence for the validity of the model. A good analogy is the leaking of a tire when it is punctured. In this case, the native patina that formed in air is the tire, and the abrasion caused the puncture. The analogy is not exact, however, since it is fair to assume that oxygen can diffuse through the native oxide, which in turn increases the internal stresses with time, which would allow more whiskers to grow when the surface is abraded multiple times.

This paper is not the first report on the formation Pb whiskers. The latter have been observed in the In–Pb system,[20] Pb thin films,[21] and in a Fe–Pb system,[22] where either the sample was strained[20] or the samples were heated.[21,22] In some cases, the temperature was increased to above the melting point of pure Pb.[22] In all these cases, however, the systems were ones in which Pb was present in high concentrations and the growth was attributed to the presence of internal residual stresses[20] or due to the melting and volume expansion of the Pb particles.[22]

The significance and health implications of the results reported herein, however, go far beyond the phenomenon of room temperature self-extrusion of a soft metal for many reasons. First, leaded brass is ubiquitous in our daily life and its consumption is on an increasing trend.[3] Second, the reproductive toxicity, neurotoxicity, carcinogenicity, hypertension causing, renal function damaging, immunodeficiency of Pb are well recognized.[4–12] Third, Pb whiskers of the sizes observed here can easily become airborne ending in human lungs.[23] This is especially true given the fragility of the whiskers and their propensity to break into smaller segments. Fourth, whiskers of the size observed in this study have been identified as carcinogens that can trigger lung and other cancers. After several decades of study, it is now appreciated that the most damaging aspect of the whiskers—the chemistries of which, in many cases such as asbestos and SiC, are benign—is their shape.[24] The fact that the whiskers observed herein are also highly toxic warrants further research into their health effects. This problem, however, may not be as severe as other whiskers because it is more likely than not that the Pb whiskers observed here would dissolve in the body and/or lungs. For example, Pb dissolution at gunshot wounds has been noted[25] and the highest Pb levels of deceased Pb smelter workers were found in the liver, followed in order of concentration by the kidneys, lungs, and brain.[8] Fifth, and maybe most importantly, is the insidious way the whiskers come to life. In essence, they lie dormant for many years and only sprout when the surface of the leaded brass, or any other alloy containing free Pb, is scratched, abraded, or polished. There is also no reason to believe that the mechanism of Pb nanowhisker growth described here is not operative in brass fittings used in potable water plumbing[13,26,27] and should be investigated.

Lastly, we are not advocating here that leaded brass is a public health hazard. For one we do not know how prevalent this phenomenon is in other leaded brasses or Pb-containing alloys, but given that oxygen is the main culprit, it is fair to assume the worst. The volumes involved are also quite small and, more likely than not, do not pose a health hazard to the general public. However, the potential harm to machinists, and other workers dealing with and abrading and/or polishing leaded brass on a daily basis such as plumbers or artisans is obvious and must be studied. The aforementioned high Pb levels measured in the brass scrap grinding shop reported 13 years ago[6] are cause for worry.

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