Limits to high vapor pressure elements in alloys for LIGO UHV components

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According to typical UHV practice alloys containing cadmium, lead, phosphorous, selenium, sulfur and zinc are not considered UHV-compatible (e.g. O'Hanlon, A User's Guide to Vacuum Technology, 2nd ed., p. 280). However, many alloys considered acceptable contain some, albeit small, levels of these elements. For example, Aluminum alloy 6061 is considered an acceptable UHV alloy by O'Hanlon and it contains a maximum of 0.25% Zn; 304 Stainless Steel contains up to 0.045% P and 0.03 % S. (In addition, of course virtually all plastics used (as a matter of necessity) have some outgassing of hydrocarbons.) In this notebook an attempt is made at setting allowable limits to these high vapor pressure elements in metallic alloys.

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Needs["PlotLegends`"]
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material compositions

stainless steel

The composition of 303 stainless steel is as follows (source is matweb.com) :
Carbon, C <= 0.150 %
Chromium, Cr 18.0 %
Iron, Fe 69.0 %
Manganese, Mn <= 2.00 %
Molybdenum, Mo <= 0.600 %
Nickel, Ni 9.00 %
Phosphorous, P <= 0.200 %[very small amount]
Silicon, Si <= 1.00 %
Sulfur, S >= 0.150 % [Note no upper limit; I couldn' t find typical values]

The percentages of the three elements of concern in the composition of 303 SE is as follows :
Phosphorous, P <= 0.200 %
Selenium, Se <= 0.150 %
Sulfur, S <= 0.0600 %

The percentages of the three elements of concern in the composition of 303 MA is as follows :
Phosphorous, P 0.0400 %
Sulfur, S 0.140 %

Type 304 Stainless steel
Carbon, C <= 0.0300 %
Chromium, Cr 18.0 - 20.0 %
Manganese, Mn <= 2.00 %
Nickel, Ni 8.00 - 12.0 %
Phosphorous, P <= 0.0450 %
Silicon, Si <= 1.00 %
Sulfur, S <= 0.0300 %

brasses

Red Brass, UNS C23000 (230 Brass), OSO70 Temper flat products

Copper, Cu	84.0 - 86.0 %
Iron, Fe	>= 0.0500 %
Lead, Pb	>= 0.0600 %
Zinc, Zn	15.0%

Low brass, UNS C24000, OSO70 Temper flat products

Copper, Cu	78.5 - 81.5 %
Iron, Fe	>= 0.0500 %
Lead, Pb	>= 0.0500 %
Zinc, Zn	20.0 %

Cartridge Brass, UNS C26000 (260 Brass), OS100 Temper flat products

Copper, Cu	68.5 - 71.5 %
Iron, Fe	<= 0.0500 %
Lead, Pb	<= 0.0700 %
Other	<= 0.150 %
Zinc, Zn	28.5 - 31.5 %

Free-Cutting Brass, UNS C36000

Copper, Cu	60.0 - 63.0 %
Iron, Fe	<= 0.350 %
Lead, Pb	2.50 - 3.70 %
Other	<= 0.500 %
Zinc, Zn	35.5 %

■ bronzes

Bronze SAE-64 composition:
Copper, Cu 80.0 %
Lead, Pb 10.0 %
Tin, Sn 10.0 %

Commercial Bronze, UNS C22000 (90-10 Bronze):
Copper, Cu 89.0 - 91.0 %
Iron, Fe <= 0.0500 %
Lead, Pb <= 0.0500 %
Zinc, Zn 10.0 %

High conductivity bronze, UNS C40500:
Copper, Cu 95.0 %
Tin, Sn 1.00 %
Zinc, Zn 4.00 %

Phosphor bronze,
The phosphor bronzes are designated as UNS C50100 through C54200. Leaded phosphor bronzes combine good strength and fatigue resistance with good machinability, high wear resistance and corrosion resistance. They are used in applications such as sleeve bearings, thrust washers, and cam followers. They are designated as UNS C53400 through C54400.
free cutting, UNS C54400:
Copper, Cu 88.0 %
Iron, Fe <= 0.100 %
Lead, Pb 3.50 - 4.50 %
Phosphorous, P 0.0100 - 0.500 %
Tin, Sn 3.50 - 4.50 %
Zinc, Zn 1.50 - 4.50 %

Phosphor bronze 1.25% Sn, UNS C50500, H02, 0.035 mm Grain Size
Copper, Cu 98.75 %
Iron, Fe <= 0.100 %
Lead, Pb <= 0.0500 %
Phosphorous, P <= 0.350 %
Tin, Sn 1.00 - 1.70 %
Zinc, Zn <= 0.300 %

Note that some of the bronze compositions have higher percentages of Zn and Pb (up to 12% in some formulations) than free-cutting, phosphor-bronze. However some of the bronze formulations have comparable percentages of these low vapor pressure elements. Phosphor bronze was approved for use in the Initial LIGO vacuum system (used for the constrained layer, damped springs in the seismic isolation system). The choice of phosphor-bronze as the spring material was based on the need for high yield stress and formability (for the coiling operation) and a stress relief temperature which is compatible with the visoelastic damping material. These springs were not vacuum baked but instead cleaned in a multi-step, acid cleaning process adapted from SLAC. The motivation for avoiding the bake was principally the low maximum temperature of the viscoelastic damping material (Dyad) in the interior of the spring (sealed by e-beam welding). However, the low vapor pressure of the Zn and Pb in the phos-phor-bronze would also preclude a bake (to prevent contaminating the bake out chamber). The phosphor bronze was considered (at the time) as acceptable since it is bound in an alloy and would not be baked in situ. However, in general it is not a good

practice to permit materials in the vacuum system which cannot be baked because it is difficult to get them as clean and because they require special processing -- which can sometimes be forgotten (and was during initial LIGO).

It is also worth noting that some bronzes are cast and castings are not permitted in the vacuum system. Moreover some bronze castings are impregnated with oil and are excellent as bearings for this reason; needless to say these formulations would be are particularly bad in a UHV application.

element data

For the molecular weight I choose S2 (disulfide) since it is the least complex gas allotrope of sulfur
I've used red Phosphorous in these calculations. White Phosphorous has a vapor pressure even higher than Sulfur. I'm not sure which allotropic form to use in the calculation.
The vapor pressures for Pb are wild extrapolations from a plot given in O'Hanlon

- **element data entry**
- **element data table**

	Atomic Wt. (g/mole)	Molecular Wt. (g/mole)	density (g/cc)	P @20C (torr)	P @200C (torr)
Cadmium, Cd	112.41	112.41	8.65	$2.\times10^{-11}$	0.0005
Lead, Pb	207.2	207.2	11.34	$1.\times10^{-18}$	$1.\times10^{-12}$
Phosphorous, P (red)	30.97	123.88	2.34	$2.\times10^{-10}$	0.04
Selenium, Se	78.96	78.96	4.79	$1.\times10^{-10}$	0.001
Sulfur, S	32.066	64.132	2.07	$2.\times10^{-6}$	2.
Zinc, Zn	65.38	65.38	7.14	$1.\times10^{-12}$	$7.\times10^{-6}$

- **primary component data entry**
- **atomic weights for primary components in allos of interest**

Fe	55.845
Cu	63.546

physical vapor deposition

- **evaporation rate**

On the issue of physical vapor deposition of Z onto our optics (and other chamber surfaces), the mass rate of evaporation is given by the Hertz-Knudsen equation (H. Lee, _Fundamentals of Microelectronics Processing_, 1989):
V [g/cm2/s] = 5.834E-2 * Sqrt(M/T) * p
where T is in K and M is the molecular weight M of element Z with p is the partial pressure of element Z (torr)

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V20C = 5.834×10^-2 Sqrt[M / (20 + 273.15)] p020C
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$$\{7.22527\times10^{-13},\ 4.90474\times10^{-20},\ 7.58494\times10^{-12},\ 3.02779\times10^{-12},\ 5.45744\times10^{-8},\ 2.75514\times10^{-14}\}$$

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V200C = 5.834 × 10^-2 Sqrt[M / (200 + 273.15)] p0200C
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$$\{0.000014218,\ 3.86066\times10^{-14},\ 0.00119406,\ 0.0000238326,\ 0.042957,\ 1.51805\times10^{-7}\}$$

■ deposition rate

The maximum deposition rate, assuming direct free-molecular streaming (no adsorption/desorption), disregarding solid angles and view factors, and no condensation rate-limited processes (if any), i.e. worst case, is then given as
rd = V*As/(Pi * r^2) [
where As is the source area and r is the distance to the target (optic). Assuming a ~10^3 cm2 source area at a distance of ~10 cm from the optic

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As = 10^3;
r = 10;
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rd20C = V20C As / (Pi r^2)
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$$\{2.29987\times10^{-12},\ 1.56123\times10^{-19},\ 2.41436\times10^{-11},\ 9.63774\times10^{-12},\ 1.73716\times10^{-7},\ 8.76989\times10^{-14}\}$$

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rd200C = V200C As / (Pi r^2)
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$$\{0.0000452574,\ 1.22889\times10^{-13},\ 0.00380082,\ 0.0000758614,\ 0.136737,\ 4.83212\times10^{-7}\}$$

given the elemental densities, the rate of deposition thickness growth (cm/s), tr, is:

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tr20C = rd20C / dens
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$$\{2.65881\times10^{-13},\ 1.37674\times10^{-20},\ 1.03178\times10^{-11},\ 2.01205\times10^{-12},\ 8.39206\times10^{-8},\ 1.22828\times10^{-14}\}$$

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tr200C = rd200C / dens
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$$\{5.23207\times10^{-6},\ 1.08367\times10^{-14},\ 0.00162428,\ 0.0000158374,\ 0.0660563,\ 6.76767\times10^{-8}\}$$

■ tolerable thickness

A.C. Tribble, B. Boyadjian, J. Davis, J. Haffner, E. McCullough, "Contamination Control Engineering Design Guidelines for the Aerospace Community", NASA CR-4740: section 2.1.3.2, "Thin Molecular Films -- Interference and Scattering" and section 2.5.3, "Optical Surface Contamination" suggests that Non-Volatile Residue (NVR) films on optical surfaces should be limited a thickness of less than 10 nm. This film thickness is the result of many potential sources of contaminant. Let's assume a maximum tolerable thickness of ~1 nm (about 1 monolayer) from any one source, then the minimum time (yr) to achieve 1 nm thickness is

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tAllow = 10^-9 × 100;
t20C = tAllow / tr20C / (365 × 24 × 3600)
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$$\{0.0119263,\ 230\,324.,\ 0.000307331,\ 0.00157599,\ 3.77855\times10^{-8},\ 0.258165\}$$

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t200C = tAllow / tr200C / (365 × 24 × 3600)
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$$\{6.06066\times10^{-10},\ 0.292614,\ 1.95223\times10^{-12},\ 2.0022\times10^{-10},\ 4.80042\times10^{-14},\ 4.68548\times10^{-8}\}$$

allowable elemental fraction in alloy

- **based on the elemental vapor pressure**
- **for solution in an alloy**

p0 is the vapor pressure over an elemental solid (or liquid in the case of S at 200C)
The vapor pressure of these elements, p, over an alloy (with c = % Se, % S, %P etc. by Wt.) will be lower than the vapor pressure, p0, over the pure element. For an ideal solution (alloy), with low molar fraction, the vapor pressure lowering is given by Raoult's law:

p = x(Z) * p0, where x(Z) is the mole fraction of the element Z

x(Z) ~ c*Ar(Y)/Ar(Z), where Ar is the relative atomic mass (gm/mole) and element Y is the dominant element in the alloy

where c is the fraction by weight of element Z in the alloy.
For stainless steel the primary element is Fe.
For bronzes, the primary element is Cu

Although I could not find a reference for the vapor pressure of these elements over an alloy, I did find a reference for Fe vapor pressure over a solid Vanadium-Fe alloy (Myles & Aldred, "Thermodynamic Properties of Solid Vanadium-Iron Alloys", J of Physical Chem, v68, n1, Jan 1964). At ~10% molar fraction, the vapor pressure is in close agreement with Raoult's law; The non-ideal deviation further lowered the vapor pressure. The vapor pressure will also be lowered by any diffusion rate limited process through the condensed solid alloy.

In the following calculations, p0 is used and then the allowable fraction of element, c, is calculated to determine the permissible amount of element Z in alloy with principle component Y.

- **calculations at 20C**
- **Allowable Percentage of Element in Alloy at a distance to the Optic of 10 cm @ 20C (1000 cm^2)**

	Fe	Cu
Cadmium, Cd	0.24	0.211
Lead, Pb	100	100
Phosphorous, P (red)	0.0017	0.0015
Selenium, Se	0.0223	0.0196
Sulfur, S	0	0
Zinc, Zn	3.02	2.66

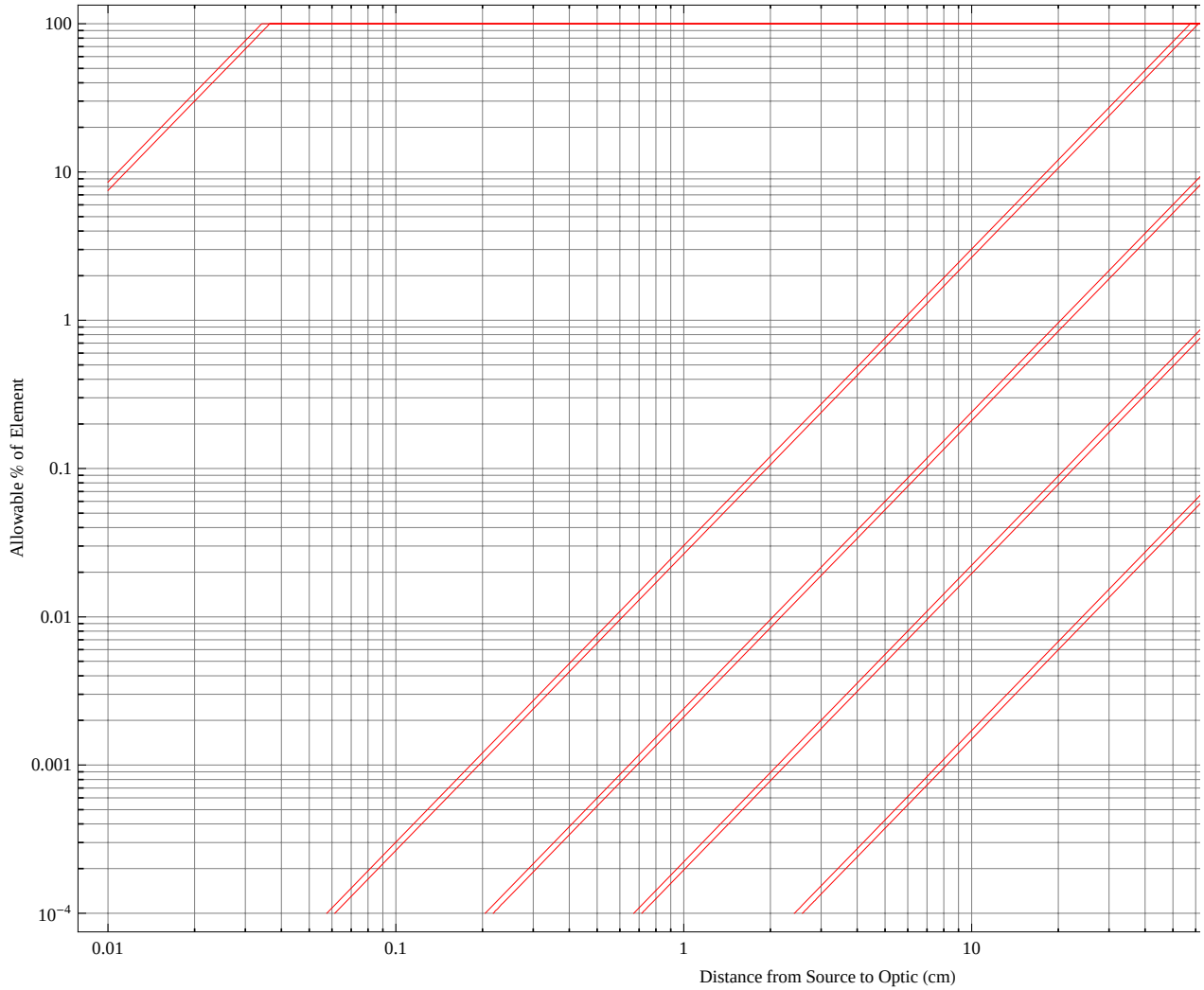
- **Allowable Percentage of Element in Alloy at a distance to the Optic of 1 m @ 20C (1000 cm^2)**

	Fe	Cu
Cadmium, Cd	24.	21.1
Lead, Pb	100	100
Phosphorous, P (red)	0.17	0.15
Selenium, Se	2.23	1.96
Sulfur, S	0	0
Zinc, Zn	100	100

- **plot calculations at 20C**

Allowable Percentage of Element in Alloy as a function of distance to the Optic @ 20C

Based on 1000 cm^2 of alloy, a maximum allowable deposition thickness of 1 nm in a period of 10 years at 20C.
The order of the curves below, from lowest to highest, is Sulfur (S), Phosphorous (P), Selenium (Se), Cadmium (Cd), Zinc (Zn) and Lead (Pb). The two curves in each set represent the element in either a Fe or a Cu alloy (and there is not much difference).



- **calculations at 200C**
- **Allowable Percentage of Element in Alloy as a function of distance to the Optic @ 200C**

None of the elements listed below (except Lead) appear to be allowable in any alloys to be baked in vacuum. As a practical matter, some small percentage of these elements are often present in UHV acceptable alloys. For example in 304L stainless steel, P <= 0.045% and S <= 0.030 %.

	Fe	Cu
Cadmium, Cd	0	0
Lead, Pb	100	100
Phosphorous, P (red)	0	0
Selenium, Se	0	0
Sulfur, S	0	0
Zinc, Zn	0	0

recommendations

1) Alloys with maximum of Cd, Pb, P, Se, S or Zn < 0.05% are acceptable for UHV service and standard vacuum bake processing.
2) Alloys with P, Se, and S > 0.05% are never acceptable.
3) Alloys with maximum of Cd, Pb or Zn <= 5% may be proposed for review by the Vacuum Review Board (VRB), with sufficient justification (i.e. no reasonable alternate materials/parts).
4) Phosphor-Bronze alloys with P <= 0.35 %, Pb <= 1%, Zn <= 1% are acceptable for UHV service at 1 m or more from any optics, with sufficient justification (i.e. no reasonable alternate materials/parts). However these parts must be air baked (not vacuum baked) and require FTIR (not RGA) qualification.

sulfur vapor pressure data

sulfur vapor pressure equation