

Subject: L080042: Is 303 stainless steel acceptable in the LIGO Vacuum system?

From: Dennis Coyne <coyne@ligo.caltech.edu>

Date: Thu, 24 Apr 2008 15:08:39 -0700

To: John Worden <worden_j@ligo-wa.caltech.edu>, Rainer Weiss <weiss@ligo.mit.edu>, Mike Zucker <mike@ligo.mit.edu>, Fred Raab <raab_f@ligo-wa.caltech.edu>, Riccardo DeSalvo <desalvo@ligo.caltech.edu>

CC: Norna Robertson <nroberts@ligo.caltech.edu>, Janeen Romie <janeen@ligo-la.caltech.edu>, Calum Torrie <c.torrie@physics.gla.ac.uk>, Justin Greenhalgh <J.Greenhalgh@rl.ac.uk>

LIGO-L080042-00

To the Vacuum Review Board (VRB):

The current LIGO Vacuum Compatible Materials List:

<http://www.ligo.caltech.edu/docs/E/E960050-B/E960050-B.pdf>

states that 303 stainless steel is acceptable. However, O'Hanlon's "A User's Guide to Vacuum Technology" clearly states that 303 should be avoided in UHV applications due to the addition of sulfur, phosphorous or selenium. In addition, the SLAC Vacuum Department Guidelines for Vacuum Systems:

<http://lhocds.ligo-wa.caltech.edu:8000/advligo/UHVWelding?action=AttachFile&do=get&target=SI>

states in section 3.1:

"Types 303, 303S, and 303Se contain excessive amounts of sulfur or selenium and are not acceptable."

It should also be noted that all of our welded vacuum chambers are comprised of 304L.

It might be argued that this prohibition is very likely due to high vapor pressure and diffusion associated with these alloys when baked to clean up the parts. Since we do not plan to do in-situ vacuum baking we might in principal get around this restriction by baking in air and performing FTIR cleanliness certification tests (rather than RGA tests). Could this approach be acceptable? A rather simplistic analysis (given below) indicates that this may not be acceptable. The exceedingly high vapor pressures for the elements Se, S and P suggest that even at room temperature there is a risk of plating optics to significant thickness in short durations.

Can we permit (continue to permit) 303 and 303 Se stainless steel into the LIGO vacuum system? One of the parts of the LLO OMC is comprised of 303 and others were called out as 300 series. Presently we are machining parts for the LHO OMC. Can we accept these parts? Should we remove 303 and 303 Se from the LIGO UHV approved materials list? This decision will have significant consequences since there are many drawings which call out 303 or 300 series SS and their are many prototype parts which have used 300 series SS. Moreover the machining costs for 302, 304 or 316 are higher.

I request a rapid reply from the VRB given the time critical nature of the OMC work for enhanced LIGO.

The simplistic analysis follows:

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 %

All rather small percentages.

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 %

Also all rather small percentages.

For the purpose of getting some idea of the potential harm of these three elements in a 303 SE alloy, let's assume ~0.2 % maximum amount by weight. N.B.: This does not allow a 303 SS, which is likely (?) to have a few % of S.

The vapor pressures of sulfur, phosphorous and selenium (over an elemental solid) are:

Po = {1e-10 Se, 2.0e-6 S, 2.0e-10 Pred) torr @ 20C

Po = {2.0e-3 Se, 2.0 S, 5e-2 P} torr @ 200C

N.B.: 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 pressure of these elements over a 303 alloy (with c = % Se, % S, %P by Wt.) will be lower than the vapor pressure over a solid of the pure element. For an ideal solution (alloy), with low molar fraction, the vapor pressure lowering is given by Raoult's law:

$$p = x(Z) * P_o, \text{ where } x(Z) \text{ is the mole fraction of the element } Z$$

$$x(Z) \sim c * Ar(Fe) / Ar(Z), \text{ where } Ar \text{ is the relative atomic mass.}$$

Ar(Z) = {78.96 Se, 32.066 S, 30.97 P, 55.845 Fe}

x(Z) = {1.4e-3 Se, 3.5e-3 S, 3.6e-3 P}

p = {1.4e-13 Se, 7.0e-9 S, 7.2e-13 P} torr @ 20C

p = {2.8e-6 Se, 7.0e-3 S, 1.8e-4 P} torr @ 200C

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.

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):

$$V \text{ [g/cm}^2\text{/s]} = 5.834E-2 * \text{Sqrt}(M/T) * p$$

where T is in K, the molecular weight M = {78.96 Se, 256.5 S, 123.9 P} and where p is the partial pressure (torr)

V = {4.2e-15 Se, 3.7e-10 S, 2.7e-14 P} gm/cm²/s @ 20C

V = {6.7e-8 Se, 3.0e-4 S, 5.3e-6 P} gm/cm²/s @ 200C

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

$$rd = V * A_s / (\text{Pi} * r^2)$$

where A_s is the source area and r is the distance to the target (optic). Assuming a ~10³ cm² source area at a distance of ~10 cm from the optic, then

rd = {1.3e-14 Se, 1.2e-9 S, 8.6e-14 P} gm/cm²/s at 20C

rd = {2.1e-7 Se, 9.4e-4 S, 1.7e-5 P} gm/cm²/s at 200C

With a Z density of {4.79 Se, 2.07 S, 1.82 P} gm/cc this corresponds to a maximum deposition rate of

{2.8e-15 Se, 5.8e-10 S, 4.7e-14 P} cm/s at 20C

{4.4e-8 Se, 4.6e-4 S, 9.3e-6 P} cm/s at 200C

If we assume a maximum tolerable thickness of ~1 nm (about 1 monolayer), then the minimum time to achieve this layer is

{9922 Se, 0.05 S, 590 P} hr at 20C

~1 sec at 200C

Obviously the vapor evolution (including diffusion out of the parent alloy) and deposition process is much more complicated, but this simple and conservative analysis leads me to the following conclusions:

- * The use of any 303 or 303-SE stainless steel should not be permitted in the LIGO vacuum system. (Perhaps in small quantity for compelling reasons and for applications distant from optics it could be permitted with a waiver.)
- * We must not bake 303 SS in a vacuum bake oven; This will cause contaminate the oven and likely contaminate subsequent loads.

Dennis