

SR Instrumentation Engineering Group Report

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Erosion/Corrosion of Machinable Tungsten in Water

Jeff T. Collins
Advanced Photon Source
Experimental Facilities Division
SR Instrumentation Engineering Group
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It was recently discovered that significant erosion/corrosion occurs with machinable tungsten when exposed to water, particularly when the water has dissolved oxygen present. The problem was first discovered about 1 1/2 years ago when extensive corrosion was found inside the cooling channels of the L5-80 white-beam slits located in sector 3-ID-A. Figure 1 and Figure 2 show cut-away sections of the tungsten slit; the water passages are severely corroded from the cooling water used to cool the slit. The problem was brought to the attention of the world's two largest manufacturers of machinable tungsten, Mi-Tech Metals from Indianapolis, IN and Kulite Tungsten Corp. from East Rutherford, NJ. Neither company had any experience with this problem and were unaware that water could cause such significant corrosion, apparently the APS was the first customer to ever use the material in this fashion.

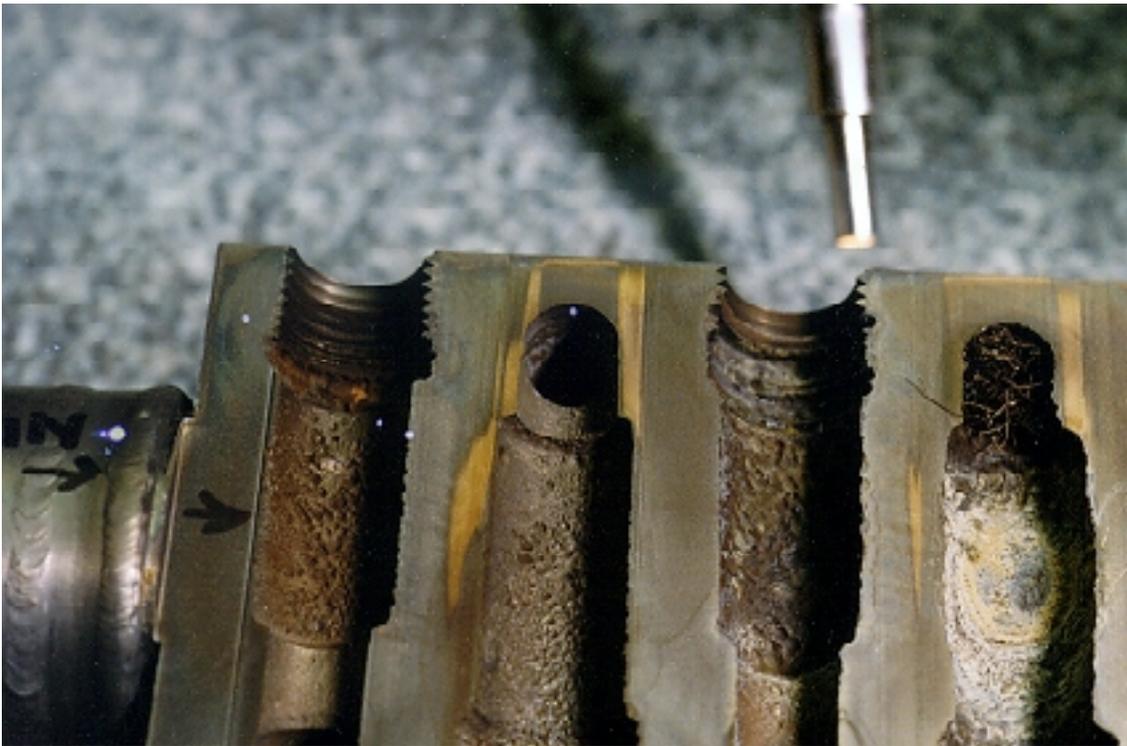


Figure 1

The machinable tungsten used in the APS slit designs consists of 95% tungsten, 3.5% nickel and 1.5% iron. The material is manufactured using a powder metallurgy process in which the constituent components are evenly mixed and then formed into billets under high heat and pressure. The nickel and iron are used to bind the matrix together, forming a very strong yet machinable material. After extensive research, it was determined that dissolved oxygen present in water reacts with the iron in the matrix forming iron oxide. The brittle iron oxide then erodes away locally leaving the machinable tungsten without a binding matrix. As this occurs, the tungsten particles erode away from the material

without a matrix to keep them bound in place. Once the erosion/corrosion process begins, it progressively accelerates as more and more surface area is exposed to the water.

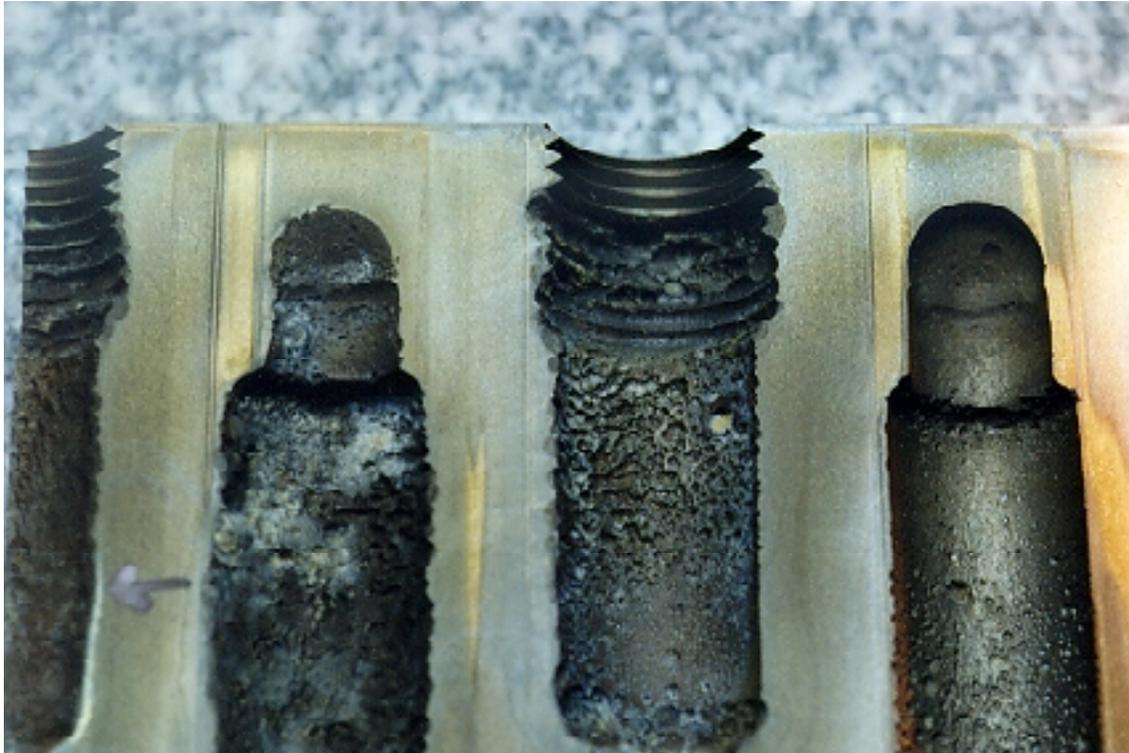


Figure 2

A test program was created to study the qualitative effects of the erosion/corrosion of machinable tungsten in water. The water utilized in the tests was de-ionized but contained levels of dissolved oxygen comparable to water used in the beamlines, approximately 4500 parts per billion (ppb) dissolved oxygen. Both Kulite and Mi-Tech suggested that electroless nickel plating of the tungsten surfaces in contact with water might prevent the erosion from starting. Thus, several test pieces were fabricated for long-term continuous-flow testing. Four samples were tested for a period of one year; two of the samples were nickel coated, and the other two samples were not coated, they were in their original machined state. Each sample contained a flow channel exact in dimensions to one of the cooling passages present in the L5-80 slit design. Each sample was subjected to 1 gpm of water flow continuously through the cooling passage, and the samples were periodically removed and weighed. The weight loss of the samples over time was recorded. Figure 3 shows the results of the non coated machinable tungsten samples. Significant weight loss occurred over a very short period, and the weight loss accelerated as more and more material was eroded away. Figure 4 shows the results of the nickel-coated samples. Initially, the nickel coating seemed to help the erosion/corrosion rate, however, after a period of time the nickel was worn away, and the erosion rate increased to the level of the non coated samples.

Non-Coated Machinable Tungsten Sample Data

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Cumulative Weight Change vs. Time

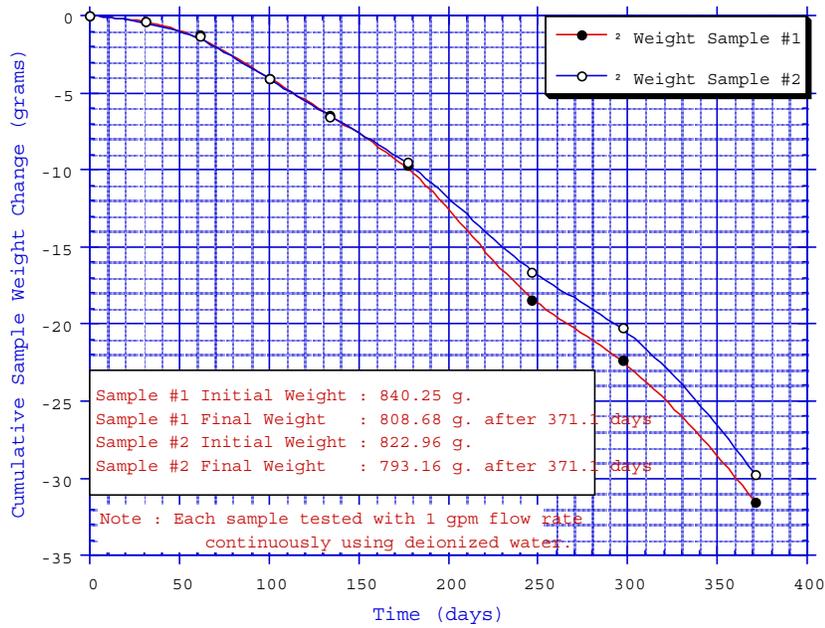


Figure 3

Nickel Coated Machinable Tungsten Sample Data

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Cumulative Weight Change vs. Time

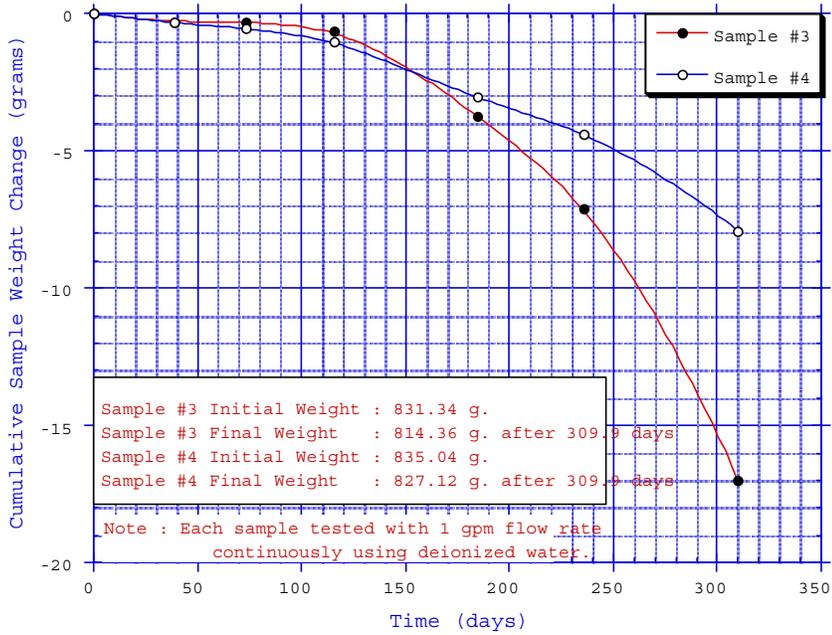


Figure 4

The weight-loss-versus-time data for the non coated tungsten samples was used to generate an equation that predicts the approximate cooling-channel hole diameter as a function of time. A simplified model was used where only the smooth initial 0.375" diameter cooling channel was considered. The weight loss was then correlated to the hole diameter increase for each set of test data, and an approximate empirical relationship was established. The relationship is given below; the hole diameter is in inches and the time is in days:

$$\text{Hole Diameter} = 78.74 \sqrt{[(2.979 \times 10^{-8}) * \text{Time} + 2.382 \times 10^{-5}]}$$

This relationship seems to hold fairly well, after one year each of the non coated samples showed an increase in hole diameter on the order of 0.09 inches with an average hole diameter of 0.465 inches. This relationship only applies to cooling channels with an initial diameter of 0.375 inches. Using this formula, one can conclude that failure will occur after approximately 3.5 years for the L5-80 slits when cooled with water that has not been scrubbed to remove the dissolved oxygen. This assumes that the cooling channel closest to the internal aperture increases in size from 0.375 inches to 0.616 inches over the 3.5-year period. When this occurs, the water will be exposed to the vacuum and failure will occur. This of course is only an estimate, however, it is clear that material erosion/corrosion occurs at a progressive rate when machinable tungsten is subjected to water with dissolved oxygen present.

The long-term solution to the erosion/corrosion problem, at least in terms of existing components that have been operational for a period of time, is to remove the oxygen from the water. This prevents iron oxide from being formed, thus corrosion and subsequent erosion are less likely to propagate without the oxidation mechanism in place. This unfortunately does not mean that the erosion process will cease. Once corrosion has started, surface areas are increased by orders of magnitude thus leaving increased areas for erosion to occur.

Although the beamline and front end de-ionized (DI) water systems were designed in such a way as to limit the dissolved oxygen concentration in the water, only recently was importance of oxygen removal from the water fully understood. Recent findings from the power-plant industries and other sources have shown that significant corrosion can still occur if there exists more than 10 ppb of dissolved oxygen in cooling water. Both ASD and XFD have been addressing this problem for separate but similar reasons. The storage ring and front-end water systems, distributed from the main utility building, have been modified to reduce oxygen concentrations to below 10 ppb. Large amounts of dissolved and free stream copper were found throughout storage ring and front-end components prior to this modification. Around the same time, it was discovered that machinable tungsten is highly corrosive in DI water with oxygen present. This was the motivation for designing a retrofit for the beamline DI pumping systems since these systems operate independently on an individual sector basis.

An economical retrofit was designed that can easily be adapted to the existing beamline pumping systems. Nitrogen bubbling and blanketing was found to be very efficient for removing dissolved oxygen. Figure 5 shows a plot of the dissolved oxygen concentration versus time for the prototype oxygen removal system adapted to the sector 3 DI pumping system. The oxygen concentration lowered from 4500 ppb to below 10 ppb in less than 15 hours. Once the oxygen has been removed, a low dissolved oxygen concentration can be easily maintained by continuously bubbling nitrogen gas through the main system reservoir. Figure 6 shows the corresponding system water resistivity versus time as the oxygen is being removed. The water quality increased from 2.5 Mohm-cm to 11 Mohm-cm in the 15 hour time span and continued to gradually improve over time until the quality was nearly 16 Mohm-cm. This directly shows the benefits of removing the oxygen from the water. As the oxygen is removed, oxidation reactions with surfaces exposed to the water are shut down, and consequently the system water quality increases since there is less load on the DI resin beds. As a result, the DI resin beds will last much longer without oxygen in the water, systems will not require as much maintenance, and beamline components will last much longer since corrosion is mitigated. Oxygen removal systems are encouraged for all existing and future water systems. The Central Shops offer a retrofit package for all existing systems and encourage the addition of this retrofit for all new systems they build.

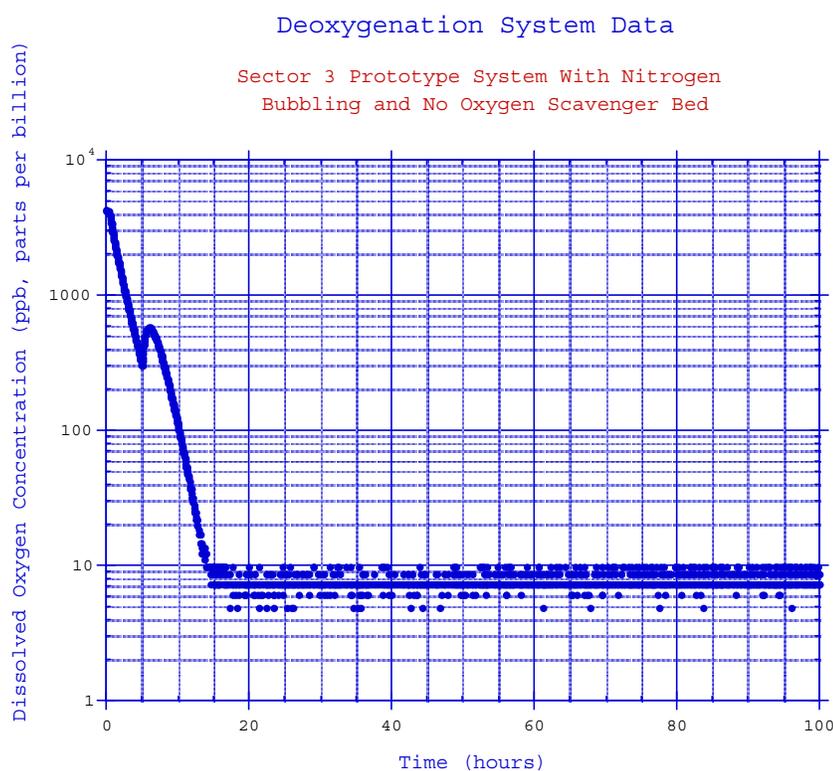


Figure 5

Deoxygenation System Data

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Sector 3 Prototype System With Nitrogen
Bubbling and No Oxygen Scavenger Bed

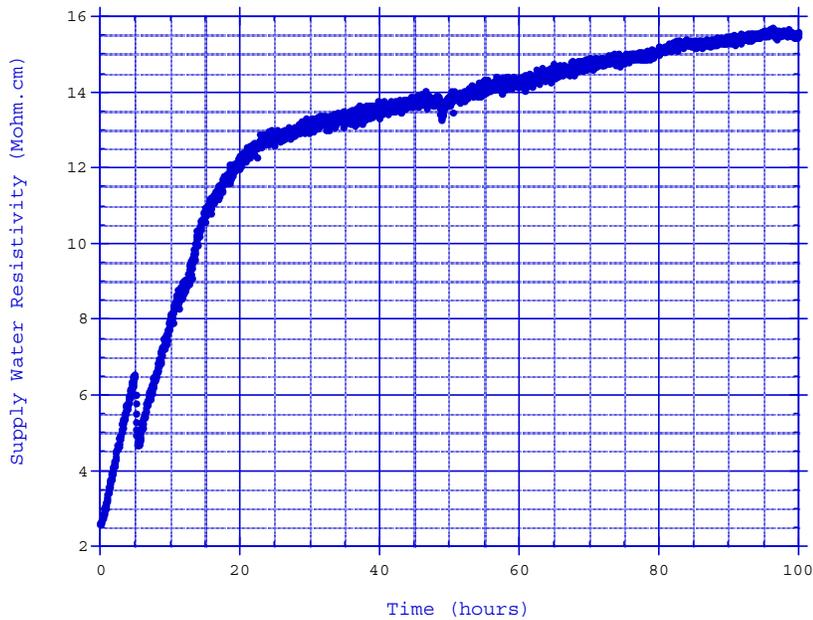


Figure 6

A best solution for new components made of machinable tungsten is to design them in such a way as to prevent water from ever coming into contact with the tungsten surface. This is the design for the new L5-92 tungsten slits, the cooling water flows through copper tubes that are brazed into the tungsten body. The L5-80 slit design has also recently been modified, the main absorber body is now made of Glidcop instead of tungsten. There are no longer any APS designs that allow water to be in direct contact with tungsten.