Van der Waals Approximation for Potassium Bubbles in Tungsten

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The finely dispersed potassium bubbles are responsible for the high-temperature sag resistance of lamp filaments; thus, the understanding of development of bubble structure is of practical importance. Usually, the ideal gas theory is used for describing the potassium bubbles in tungsten. Instead, we used the van der Waals approximation which can account for phase changes and describes a two-phase coexistence region. It is shown theoretically that bubbles in the practically important size range (some tenth of microns) can exist in a two-phase state. Some experimental findings are also better explained by the real gas approximation.

I. INTRODUCTION

The most important component of an incandescent lamp is the filament which is made from tungsten wire. The processing of tungsten wire is made basically after the patent of Coolidge[1] even in our days. The process involves powder sintering and thereafter the thermomechanical treatment of the sintered ingot. The ingots are rolled or swaged and subsequently drawn into fine size wire. There are several heat treatments for recrystallization and/or stress relief, as well. Depending on rod/wire diameter, working temperatures vary from 2000 to 800 K, where the higher value applies for the initial steps (thicker rod) and the lower one for the fine size (10 to 50 μm in diameter) wires. Details of the process are described in References 2 and 3.

To maintain adequate high-temperature strength of tungsten lamp over a long period of time, K, Si, and Al are added in small amounts (typically in tens of parts per million). From these dope elements, potassium is the most important additive. Recrystallization of a potassium doped tungsten wire results in a particular structure consisting of long overlapping grains. This is the structure which is sag resistant—the most important requirement for filaments operating at high temperatures.

Although on the basis of an empirically developed technology, potassium doping is used from 1922,[4] the first theoretical explanations about the role of potassium in tungsten originate from the year 1972.[5,6] This role can be summarized as follows. Since potassium is insoluble in tungsten, at the end stage of the sintering process, potassium is closed in pores of diameter 0.1 to 1 μm. As the critical temperature of potassium, 2281 K,[7] is lower than the sintering temperature (≈3200 K), the potassium is in gas phase during sintering. Applying the ideal gas model, the equilibrium bubble diameter, \( d \), can be calculated from the balance between Laplace pressure (resulting from the curvature of the bubble) and the gas pressure:

\[
\frac{3nRT}{2\pi \Gamma} \leq d
\]

where

\[ n = \text{the number of moles of potassium in the bubble;} \]
\[ R = \text{the ideal gas constant;} \]
\[ T = \text{the absolute temperature; and} \]
\[ \Gamma = \text{the surface energy of tungsten.} \]

It is assumed[9] that during the mechanical working (rolling, swaging, and drawing), the shape change of potassium bubbles is identical to that of the rod or wire, and the initially spherical bubble will reach an ellipsoidal shape after deformation. Therefore, the greater is the deformation, the more is the elongation of the bubbles. Above a critical length-to-width ratio (aspect ratio), the ellipsoids become unstable. This critical aspect ratio is 8.89.[8] During a process heat treatment, each unstable ellipsoid breaks up into a string of small spherical bubbles. The greater is the deformation (and, hence, the greater is the aspect ratio of the ellipsoids), the greater is the number and the smaller is the size of the broken up bubbles. This particular array of the small potassium bubbles represents a barrier against grain boundary movement during recrystallization and this is why long elongated grains are formed.

During planning of the thermomechanical process, the aforementioned issues must be taken into account. For instance, if process heat treatments are applied too often, the ellipsoids cannot reach the critical aspect ratio (because of the little plastic deformation), and the heat treatment will not break up the ellipsoids but will spheroside them.

Based on the original work of Moon and Koo,[8] Vukcevich[9] made detailed calculations on bubble development in tungsten during thermomechanical process steps. He used ideal gas theory to obtain the equilibrium size of the bubbles at the end of sintering and assumed that the potassium is in gas state even during process steps. Though the pore size in ingot has a fairly broad distribution, one can say that the calculated and measured bubble sizes are in good agreement in the case of thicker (\( d > 0.9 \) mm) wires. However, bubbles in thin wires are much greater than calculated from Vukcevich’s model.[10]

This work was motivated by the practical importance of size distribution of potassium bubbles. We tried to find at least a qualitative explanation why Vukcevich’s model fails at smaller wire sizes. Our aim was to investigate whether the main assumption, viz. that the potassium is in gas state, is valid. Since process temperatures are well below the criti-
Fig. 1—(a) Ideal and (b) van der Waals gas pressure (solid lines) for \( n = 1.8 \times 10^{-15} \text{ mol} \) potassium and Laplace pressure (dotted lines) vs bubble diameter. For these big bubbles, there is no difference in equilibrium bubble size between the two gas models.

**II. VAN DER WAALS EQUATION FOR POTASSIUM**

The well-known van der Waals equation of state is given by Eq. [2]:

\[
(p + \frac{an^2}{V^2})(V - nb) = nRT
\]

where \( p, V, n, \) and \( T \) are the pressure, volume number of moles, and temperature of gas, respectively.

For a given \( T \), this equation represents a third-order curve in the \( p-V \) space. If \( T = T_c \), this curve has an inflexion point at \( V = V_c \) and \( p = p_c \) (at the critical point), where

\( T_c \) is the critical temperature; \( p_c = 16.2 \text{ MPa} \) is the critical pressure; and \( V_c = 5.32 \text{ cm}^3/\text{g} \) is the critical specific volume.

The parameters \( a \) and \( b \) can be determined by fitting Eq. [2] at the critical point using two of the three critical constants. With \( T_c \) and \( p_c \), one obtains

\[
a = \frac{27}{64} R^2 \frac{T_c^2}{p_c} = 9.366 \text{ Nm}^4 \text{ mol}^{-2}
\]

\[
b = \frac{R}{8} \frac{T_c}{p_c} = 1.463 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}
\]

Using these constants, Eq. [2] can be displayed for various temperatures for different amounts of potassium as \( p-V \) curves. Of course, instead of bubble volume, the directly measurable bubble diameter can also be used.

We are interested in the equilibrium bubbles at high (sinter and process heat treatment) temperatures, whose experimentally observed sizes range from about 200 Å to 2 \( \mu \text{m} \).

The gas pressure is opposed by the Laplace pressure:

\[
\frac{4\Gamma}{d}
\]

where \( \Gamma \) is the surface energy of tungsten \((0.5 \text{ J m}^{-2} < \Gamma < 2.5 \text{ J m}^{-2})\). Therefore, we displayed Eq. [2] for those potassium contents, where the intersection of isotherms and the Laplace pressure (Eq. [5]) is in the aforementioned size range. Figures 1(a) through 6(a) show \( p-d \) curves \((d\) is the diameter of the bubble\) calculated from the ideal gas theory, while Figures 1(b) through 6(b) show those calculated from the van der Waals equation of state (Eq. [2]). Laplace pressures are also depicted for \( \Gamma = 1 \text{ J m}^{-2} \) and \( \Gamma = 2 \text{ J m}^{-2} \) with dotted lines.

Of course, equilibrium bubble size is given by the intersection of curves for the gas pressure and for the Laplace pressure. In certain circumstances, the intersection is in the two-phase region of the van der Waals curves. This is most pronounced in Figure 2(b) \((n = 1.8 \times 10^{-16}, T < 2200 \text{ K})\).

However, as we will see in Section III, this does not represent a stable equilibrium point.

**III. STABILITY OF EQUILIBRIUM BUBBLE SIZE AND EXISTENCE OF TWO-PHASE BUBBLES**

The equilibrium bubble size always represents a stable equilibrium in the ideal gas model, because the gas pressure curve has a greater slope than the Laplace pressure. Thus,