Model for Grain Growth in AMTEC Electrodes

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ABSTRACT

The power produced by an AMTEC is dependent on the porosity of the electrode layers deposited on the surface of the BASE tubes. The elevated temperatures at which these power generators operate result in a slow growth or coalescence of the grains that comprise the electrode layers thereby reducing porosity and effective surface area. The lifetime of AMTEC electrodes is therefore related to the rate of grain growth of the electrode material. A preliminary model has been developed to determine the rate of grain growth over the operational lifetime of an AMTEC. This model examines the conditions for continuous growth as a function of the relative sizes, boundary and activation energies and mobilities of the grains. An assumption of strain-free growth has been made in determining the factors for normal growth. Experimental measurements for titanium nitride alloy electrodes are compared with this model. Predictions are made for performance lifetimes out to 10 years.

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INTRODUCTION

Alkali metal thermal-to-electric converters (AMTEC) are baselined for use on several planned outer planetary missions. A necessary requirement is that they are capable of operation from 7 to 15 years. Key to the performance of the AMTEC are the Beta Alumina (β" Alumina) Solid Electrolyte (BASE) ceramic ionic conductor tubes and the porous electrodes deposited on the inner and outer surfaces. The power conversion process is largely driven by the properties characteristic of the ceramic BASE material and the associated electrode layers. The electrodes are positioned on the inner and outer BASE tube surfaces to collect the electrons and ions separated by diffusion of ions through the ionic conductor. The apparent charge transfer characteristics are determined in part by the porosity of the electrodes. This porosity is effected by the extended exposure of the electrodes to the high operational temperatures (e.g. 700 to 850 C).

The porous electrode surface is composed of amorphous and polycrystalline grains that increase in size due to diffusion of material between neighboring grains. This grain growth results in the slow reduction in available surface area on the electrode and causes degradation of electrode performance. Usually this process continues to a point where the grains reach a critical average size and pseudoequilibrium is attained where the surface energies related to the tensions between the grains becomes mutually balanced. In such a case the grain size would remain relatively constant or increase very slowly under continued isothermal conditions. This process is generally referred to as normal or continuous grain growth. Another name for this type of growth is normal coarsening or coalescence. In some cases, when there is significant difference in the initial grain sizes or when impurities are present, growth can continue in such a way that much larger grains will continue to grow at the expense of adjacent grains. In such cases, the growth is considered abnormal, discontinuous or exaggerated. The model under development in this paper will initially focus on normal growth.

GRAIN GROWTH MODEL DEVELOPMENT

Present theories of grain growth propose the kinetics to be determined by the velocity or net motion of the adjacent grain boundaries with respect to each other. This velocity can be considered as proportional to the pressure difference or driving force at the grain boundary with a proportionality constant that can be related to a mobility factor [1].

$$V = MP \tag{1}$$

If the average grain radius is R and γ_b is the average grain boundary energy, then the pressure difference can be approximated by

$$P = \gamma_b / R \tag{2}$$

The assumption of a uniform grain boundary energy was successfully used by others [2] and is justified for an unstressed surface layer. The boundary velocity then becomes [2,3]

$$V = dR/dt = MP = M \gamma_b / R \tag{3}$$

The solution of this equation is

$$R^2 - R_o^2 = 2 M \gamma_b t \qquad (4)$$

where Ro is the average initial grain radius.

Although the dependence on the "squared" growth exponent results from this derivation, the actual pressure difference at the grain boundary has a more complex dependence on the surface and volume energies at the grain boundary resulting in higher order dependencies on R. The results of other researchers have shown that a more generalized solution is [3]

$$R^n - R_o^n = c M \gamma_b t \qquad (5)$$

where c is a proportionality constant that provides for correct dimensionality. For simplicity, the factor of 2 has been included in c.

For surface diffusion across a highly irregular surface, the adjacent boundaries of the grains can be considered generally high angle. This means that the included angle between the grains is large. The mobility of high angle grain boundaries has been found to generally obey an Arrhenius type relationship to an activation energy E_A for boundary migration of the form [4]

$$M = M_o \exp(-E_A / RT) \qquad (6)$$

The solution to equation 3 takes on the form

$$R^n - R_o^n = c \gamma_b t M_o \exp(-E_A / RT) \qquad (7)$$

To determine the grain boundary energy the interface between the grains can be thought of as a thermal groove with an angle ϕ arising from a balance of forces due to surface tension and pressure at the grain boundary [5]. Figure 1 depicts such a groove. The boundary energy can be determined by equating it to
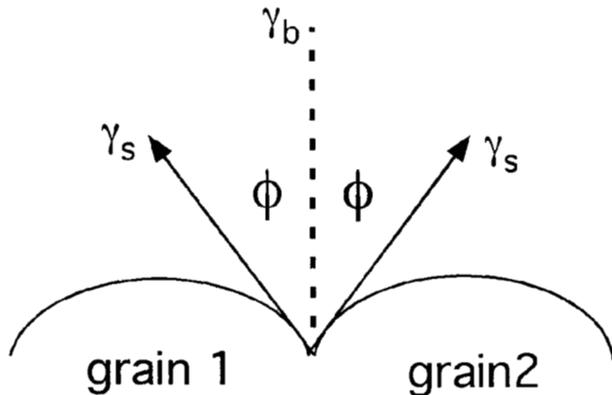

Figure 1. Boundary and surface energies at a thermal groove.

sum of the components of the surface energy of the grains at the interface [5]. The boundary energy then becomes

$$\gamma_b = 2 \gamma_S \cos \phi \qquad (8)$$

Including the expression for γ_b, equation 7 becomes

$$R^n - R_o^n = c M_o \gamma_S \cos \phi \, t \exp(-E_A / RT) \qquad (9)$$

or

$$R = R_o \left(1 + c M_o R_o^{-n} \gamma_S \cos \phi \, t \exp(-E_A / RT)\right)^{1/n} \qquad (10)$$

Again, the factor of two has been adsorbed into the constant c for simplicity.

In order to apply this equation to results for TiN, which is one of the primary electrode materials used in the AMTEC under development for the U.S. space program, growth characteristics need to be selected related to this material. The growth exponent, n, has been determined to be between 3 for particle growth controlled primarily by volume diffusion and 4 for surface diffusion at the grain boundaries [3]. While no results for n are available for TiN, data for two associated alloys, TiMn and TiV, have produced an average value of 3.8 for bulk material tending to 3.2 for surface diffusion dominated growth [6].

The values used for TiN in order to compare the model with the actual measured data are listed in Table 1. These values are only considered characteristic ones in that they have been obtained for TiMn and TiV alloys and TiN chemical vapor deposition data. In addition, the energy values are assumed constant for this preliminary model but are expected to have some variation with temperature and possibly time.

Table 1. Estimated TiN model parameters

Parameter	Estimated Value	
n	3.2	[6]
γ_S	230 kJ/mole	[7]
E_A	175.5 kJ/mole	[6]
ϕ_S	30 degrees	
ϕ_L	40 degrees	

The groove angles for the small and large grains, ϕ_S and ϕ_L, were determined as average values by inspection of scanning electron microscope (SEM) photos of the initial electrode surfaces.

The experimental data for TiN grain growth has been compiled from three isothermal exposure tests of BASE tubes of the same configuration as used in AMTEC cells. The exposure tests were conducted in a low pressure sodium vapor representative of operational AMTEC conditions for various times. Each test resulted in a single grain growth measurement. The individual tests ranged from 1120 K to 1220 K and from 500 to 1800 hours so in order to present the data as a function of time for comparison with the model an average temperature value of 1170 K has been used. The grain sizes were determined by examination using a SEM. The grains were segregated into small and large grains to aid in resolving changes in the growth rate. The ranges of large and small grain sizes were measured from SEM photos of different magnification. Figure 2 compares the model results with the measured TiN grain sizes. Since the mobility coefficient is not known the
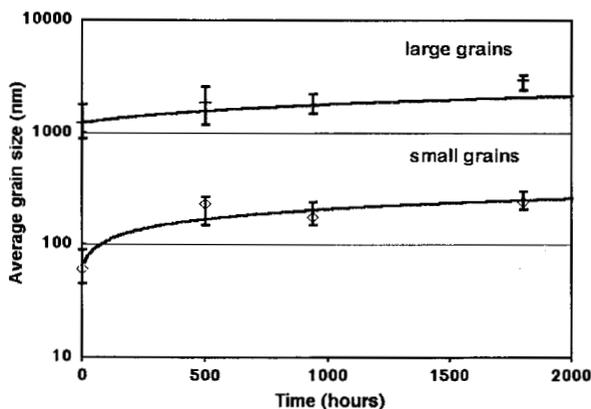

Figure 2. Model results compared to growth of large and small TiN grain sizes over 1800 hours.

model was first fitted to the small grain size data by adjusting the value of the constant factor of the exponential term within equation 10. The comparison for the larger grains was made by ratioing the relative cos ϕ values at the grain boundaries and that of the initial grain sizes, R_0, for the small and large grains and adjusting the model accordingly. The adjustment factor for the second term inside the parentheses in equation 10 is then

$$\frac{\cos\phi_L}{\cos\phi_s}\times\left[\frac{(R_0)_s}{(R_0)_L}\right]^n \qquad (11)$$

The model results are observed to be comparable to the measured ones for both small and large grains. The model results indicate that the grain growth rate decreases after an initial period. This result might imply that the grain growth rate would decrease with time so that the grains would tend to a critical size without further electrode performance degradation.

Figure 3 depicts the results for the present model out to 10 years. The calculation indicates a growth rate that

tends to a relatively constant value after an initial decrease. After 10 years the model indicates a maximum average grain size of about 7 to 8 microns. The model however doesn't include the effects of impurities within the electrode material. The presence of impurities can either enhance nucleation or can have the effect of pinning the grain boundaries and reducing the rate of grain growth.
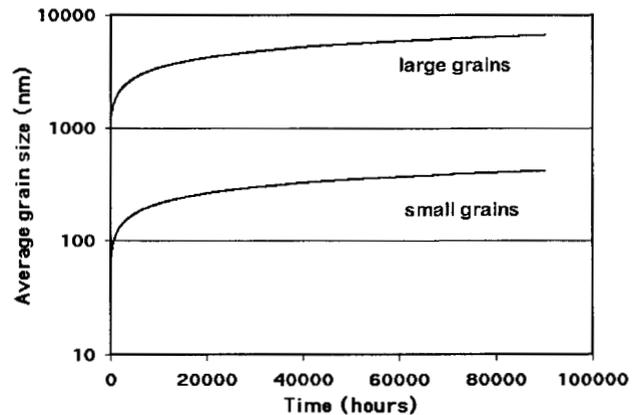

Figure 3. Model projections for grain growth rates out to 10 years.

CONCLUSION

The present model for AMTEC electrode grain growth displays values that are comparable to measured data for TiN. The present available measured grain growth data for TiN however is still limited which hinders the ability to project long term effects. The extended growth rate projection will need to be supported by longer term test data than the 1800 hours presently available. The present results do indicate that the long term performance of TiN electrodes can be modeled. Although the model has been used for TiN electrodes the derivation does not limit its application only to this material.

ACKNOWLEDGMENTS

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