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Activation Energy for Grain Growth in Bismuth Coatings

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ABSTRACT

The knowledge of both activation energy and diffusion coefficient is needed for a predictive processing of grain size in coatings. However, for metals as Bismuth there is insufficient information available in the literature for these parameters. To determine these values, a method is adopted wherein an examination of the grain size is conducted for coatings deposited isothermally. The exponent for grain growth with time is determined, thereby enabling quantification of the activation energy and diffusion coefficient. Bismuth coatings that range from 10 μm to 1 mm thick are deposited using electron-beam evaporation onto temperature-controlled substrate surfaces of glass and lithium fluoride. The grain size of each coating is measured upon examination of the microstructure in cross-section using the intercept method. Ideal grain growth is observed over the experimental range of deposition temperatures examined from 317 to 491 K. The activation energy (Q) for grain growth in bismuth is fit as $0.47 \text{ eV}\cdot\text{atom}^{-1}$ with a diffusion coefficient (D_0) of $3.3\times 10^{-4} \text{ cm}^2\cdot\text{sec}^{-1}$.

Keywords: Bismuth; Coatings; Diffusion; Evaporation

INTRODUCTION

The synthesis of fully dense coatings to millimeters, in thickness in the form of free standing foils and as coated substrates, is of growing interest for material behavior studies under dynamic loading conditions. In particular, it is of interest for bismuth, to assess the phenomena of melt refreeze [1-2] and to determine the kinetics of polymorphic phase transitions within bismuth under high pressure [3-4]. To pursue the controlled growth of specimens with grain sizes that range from 0.1 μm to 1 cm presents a challenge that is met [5] by the preparation of coatings using physical vapor deposition technology. The use of electron-beam evaporation [6] is an established and appropriate process to systematically deposit such thick coatings as high deposition rates in excess of $0.1 \mu\text{m}\cdot\text{s}^{-1}$ can be routinely achieved. The classic zone model(s) for growth of vapor deposits [7-11] provide an excellent starting point for selecting the process conditions required to produce dense metal coatings. For the case of evaporative deposits [11], it is primarily the surface and bulk diffusion processes that progressively affect grain size growth with increasing temperature from dense columnar-type microstructures to equiaxed polycrystalline solids. Within this context, we investigate the electron-beam evaporation conditions relevant to the formation of bismuth deposits to determine the activation energy (Q) for growth and the diffusion coefficient (D_0).

It is well known that the time at temperature affects the grain size during the deposition process. In order to quantify the kinetics of grain growth, the coating temperature during the deposition process should be nearly isothermal. There appears to be no reference data available in the literature for self-diffusion in bismuth. Thus we present new experimental results for the time evolution of grain size from the 10^{-1} -to- $10^2 \mu\text{m}$ scale for the electron-beam deposition of bismuth coatings up to 1 mm in thickness. The kinetics is evaluated with respect to the grain growth law. Analysis of the activation energy and the mechanism for grain growth is made for

temperatures above half the melt point (T_m), i.e. greater than room temperature and up to near the ambient-pressure melt point of 544 K.

EXPERIMENTAL METHODS

The electron-beam evaporation method is used to produce a large range of grain size (d_g) in the deposited coatings. The vacuum chamber is cryogenically pumped to a base pressure less than 1.3×10^{-5} Pa. A 0.9994 pure bismuth target is melted using an electron-beam operated at 10 kV with a 0.2-0.6 A discharge current. The source material is evaporated in two forms: as 2-to-15 mm pieces in a 40 cm^3 pocket-crucible; and as 2 cm diameter by 15 cm bar using a rod fed source. The source-to-substrate distance range of 10-15 cm facilitates higher deposition rates for the synthesis of thick coatings. The 18 mm diameter by 7 mm thick glass substrates are directly heated by illumination from a 1 kW quartz lamp. The 3 mm sq by 0.5 mm thick lithium fluoride substrates are conductively heated by attachment to a tantalum plate that is resistively heated using a boron-nitride heating element. The calibrated deposition rate is monitored in-situ using a 6 MHz gold-coated oscillating quartz crystal.

The baseline temperature of the substrate holder is regulated through feedback-control. However, it's the actual temperature of the coating that needs [5] to be measured for determination of the grain growth kinetics. For this purpose, thermocouples are placed in firm contact with substrate surface. As the deposition process proceeds, the substrate surface thermocouples are embedded into the coating. This method of measurement provides the actual coating temperature (T_c) during the deposition process which will vary from the reference of the substrate holder.

The columnar microstructure of the bismuth coating is imaged in the cross-section of polished samples using optical and scanning electron microscopy. The method of x-ray diffraction (XRD)

provides a measure of the crystalline orientation of the grains in the bismuth coatings. The coating surfaces are scanned in the $\theta/2\theta$ mode using Cu $K\alpha$ radiation. The grain size (d_g) is computed as the average column width that is measured from the cross-section images. The lineal intercept method provides a measure of the average spacing between the columnar grain boundaries.

RESULTS & ANALYSIS

The micrographs of the Bi coatings reveal the basic features of the microstructure. An optical micrograph of a typical cross-section using polarized light is shown in Fig. 1. The grain boundaries, clearly present for this 437 K deposit, typify the zone 2 growth [7, 9, 11] of a vapor deposited coating. The growth is columnar, fully dense, with several grains along the growth direction. This zone 2 type microstructure is expected for the 317 to 491 K experimental range of coating temperatures that exceed $0.58 \cdot T_m$ of Bi. The cross-section images are then used for measuring d_g which equals $26.6 \pm 1.4 \mu\text{m}$ for the Bi coating of Fig. 1.

The XRD scans of the Bi coatings reveal an invariant $\{003\}$ rhombohedral texture as seen in (Fig. 2) the representative $\theta/2\theta$ scan for a 435 K deposit. The rhombohedral unit cell for Bi has lattice parameters [12] of $a=b$ equals 0.4547 nm and c equals 1.1862 nm with $\alpha=\beta$ equals 90° and γ equals 120° . The only peaks observable (in Fig. 2) are the (003), (006), and (009) Bragg reflections at measured 2θ positions of 22.4° , 45.8° , and 71.4° , respectively.

An analysis of grain growth is made since the d_g of the Bi coatings is measured as a function of constant coating temperatures (T_c) during depositions over well-defined time intervals (t). The grain growth law provides the relationship to compute the activation energy (Q) needed for grain growth during deposition of the Bi coatings. The grain growth law [13] relates grain size (d_g) as proportionate to time (t) raised to the power (n). The exponent (n) equals one-

half for the condition of ideal grain growth. To determine the exponent for Bi grain growth, the d_g is plotted (in Fig. 3) versus t^n . The grain size data sets (at a T_c of 331 K as well as 427 K) illustrate the linear relationship that is indicative of ideal grain growth (n equals 0.5) in these Bi coatings. Ideal grain growth is generally observed [5] in other electron-beam deposited coatings as well as for aluminum. In this plot, the grain size (d_g) is determined from the expression

$$d_g^2 = [d_g(f)]^2 - [d_g(i)]^2 \quad (1)$$

where $d_g(i)$ is the initial grain size and $d_g(f)$ is the final grain size. For these as-deposited coatings, $d_g(i)$ equals zero.

The evolution of grain size with time at temperature is observed (as seen in Fig. 3) to follow ideal grain growth. Therefore, a linear variation of T_c^{-1} versus $\ln(d_g^2 \cdot t^{-1})$ will result [13-14] as is seen in Fig. 4 for the present case of Bi. The activation energy (Q) for grain growth is then determined [13-14] from the slope of this linear relationship, which equals $\{-Q \cdot (R)^{-1}\}$ where R is the molar gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$). That is, the activation energy (Q) is determined from the relationship,

$$Q = -R \cdot \partial[\ln(d_g^2 \cdot t^{-1})] \cdot \partial[T_c^{-1}]^{-1} \quad (2)$$

A linear regression analysis is used in the (Fig. 4) data plot “ $10^3 \cdot T_c^{-1}$ vs. $\ln(d_g^2 \cdot t^{-1})$ ” to compute Q which equals R multiplied by the slope of the linear regime. The activation energy (Q) equals $0.47 \text{ eV} \cdot \text{atom}^{-1}$ ($44.8 \text{ kJ} \cdot \text{mol}^{-1}$). An interpolated intercept value (at T^{-1} equals zero) for $d_g^2 \cdot t^{-1}$, i.e. the diffusion coefficient (D_0), is then determined equal to $3.3 \times 10^{-4} \text{ cm}^2 \cdot \text{sec}^{-1}$.

For comparison to the value determined from grain growth, an activation energy of $0.8 \text{ eV} \cdot \text{atom}^{-1}$ ($77 \text{ kJ} \cdot \text{mol}^{-1}$) is determined from the Van Liempt relation [15] of $Q = 0.142 T_m$ (in units of $\text{kJ} \cdot \text{mol}^{-1}$) for normal self diffusion. Although the grain growth study is conducted over the temperature range of $(0.58-0.90) \cdot T_m$, it is possible that the mechanism for diffusion under

study (i.e. grain boundary) may be less than for the bulk diffusion process. In a compilation of findings by Martin and Perrailon [16], they note for the case of self-diffusion that the apparent activation energy in a grain boundary is roughly 0.4-0.6 times the activation energy for bulk diffusion. The Q of Bi for the present study fits this comparison as it is 0.59 times the value given by the Van Liempt relation.

CONCLUSIONS

A grain size dependence on the coating temperature with respect to the melt point (T_m) is found for the evaporative deposition of bismuth. Ideal grain-growth behavior is observed in coatings over the temperature range of $(0.58-0.90) \cdot T_m$. With measurement of the coating temperature and grain size, we've determined the activation energy for grain growth in bismuth as $0.47 \text{ eV} \cdot \text{atom}^{-1}$. The value is consistent with a self diffusion mechanism for grain boundaries.

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FIGURE CAPTIONS

- Figure 1. The optical micrograph of a polished bismuth coating as viewed in cross-section that was deposited at 437 ± 1 K.
- Figure 2. A plot of intensity versus 2θ position, in this x-ray diffraction scan of a coating deposited at 435 ± 5 K, reveals the $\{003\}$ texture of rhombohedral bismuth.
- Figure 3. The linear curves of grain size (d_g) versus square-root of time ($t^{0.5}$) confirm the assumption of ideal grain growth over the full temperature range measured for the bismuth coatings during electron-beam deposition.
- Figure 4. Linear fits to the curves in the plot of $10^3 \cdot T^{-1}$ versus $\ln(d_g^2 \cdot t^{-1})$ follows the assumption of ideal grain growth for these bismuth coatings.

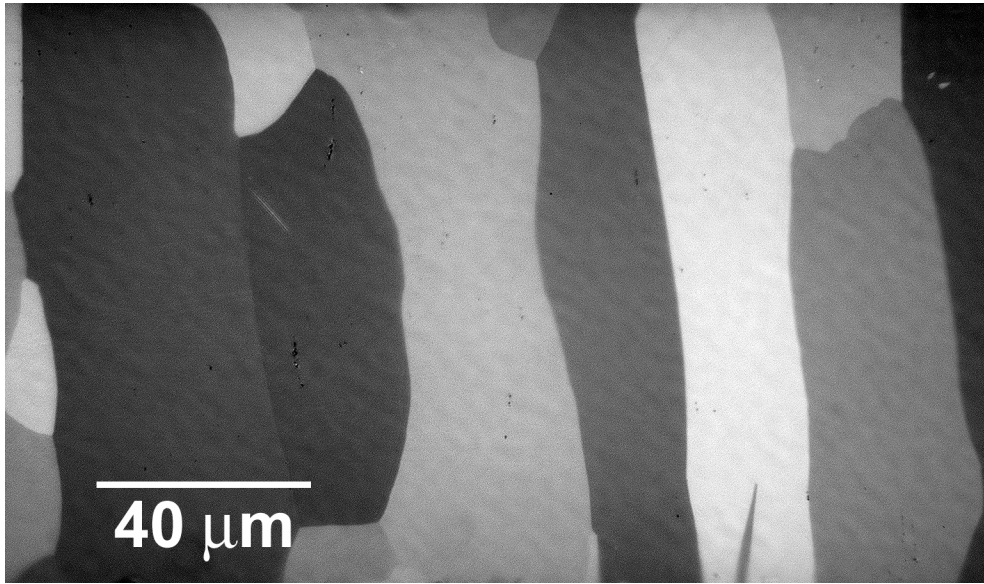


Figure 1.

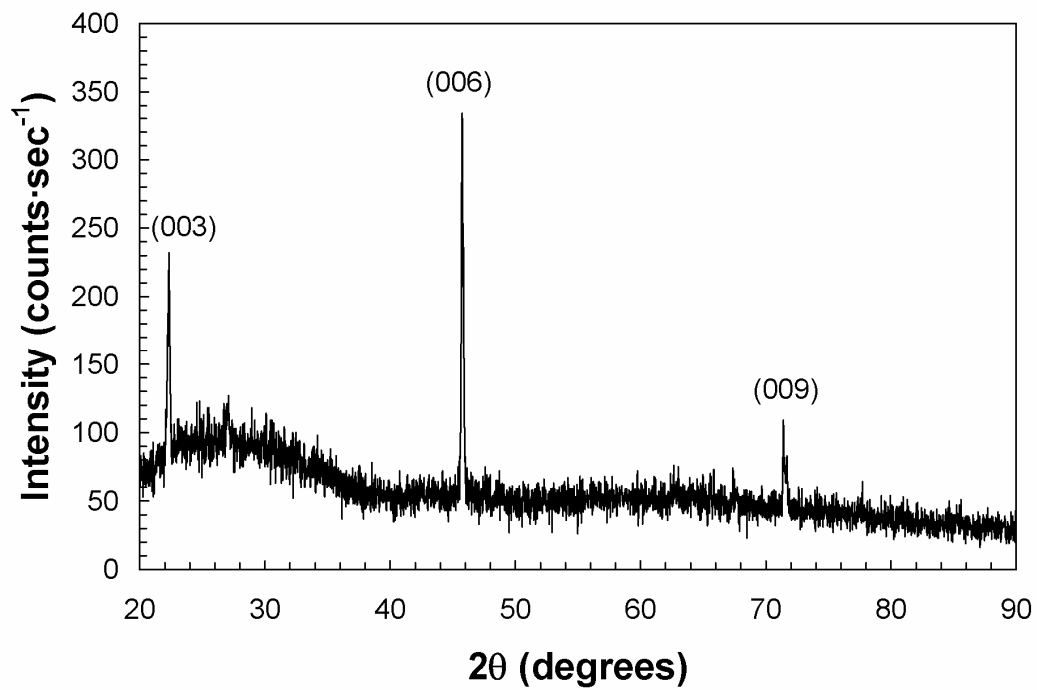


Figure 2.

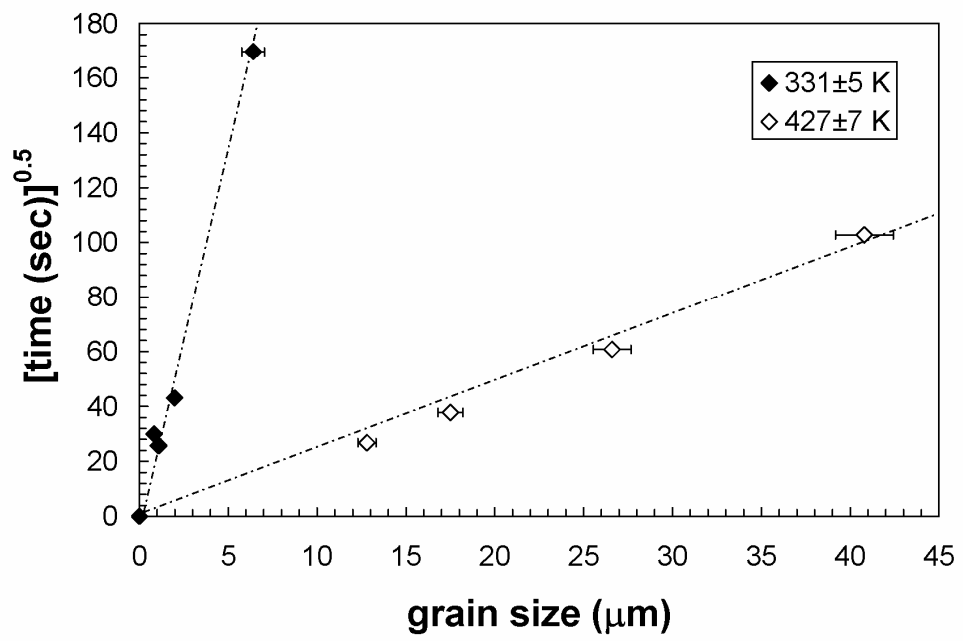


Figure 3.

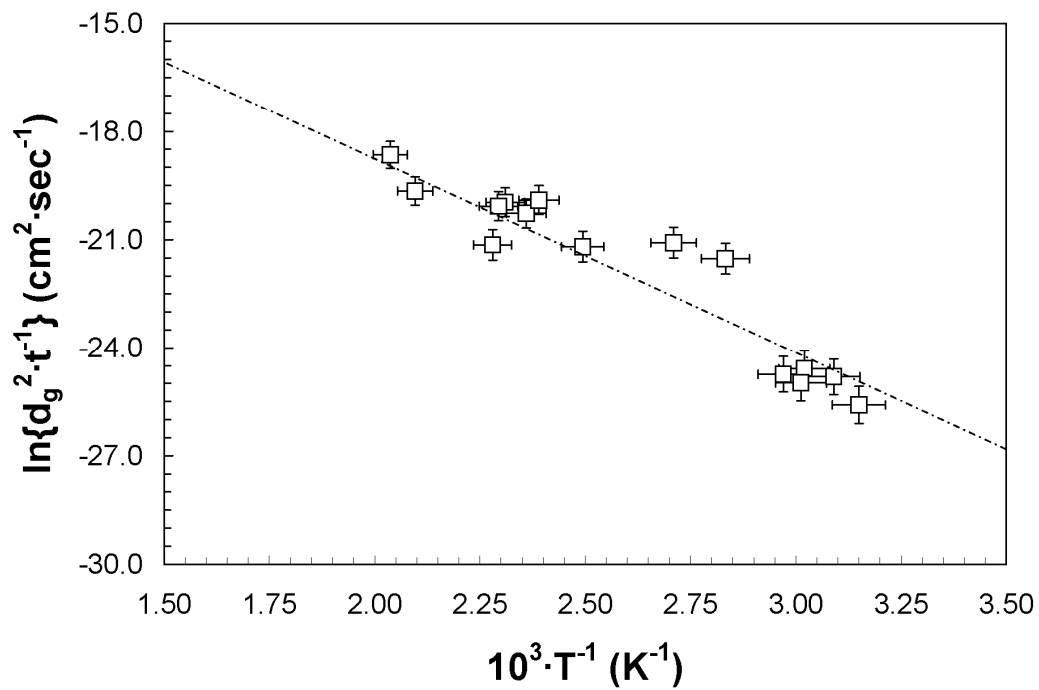


Figure 4.