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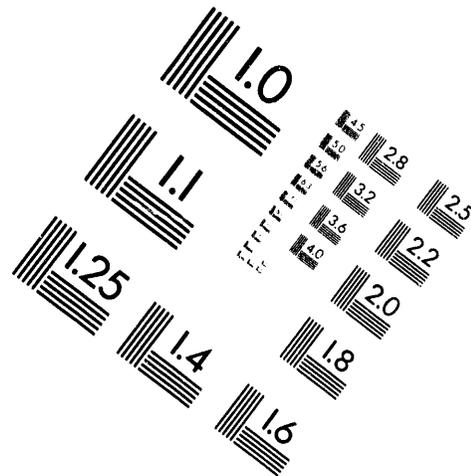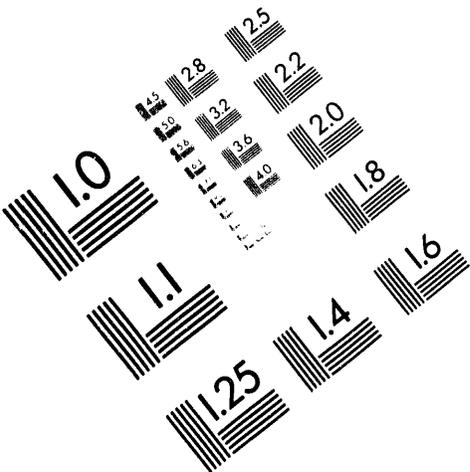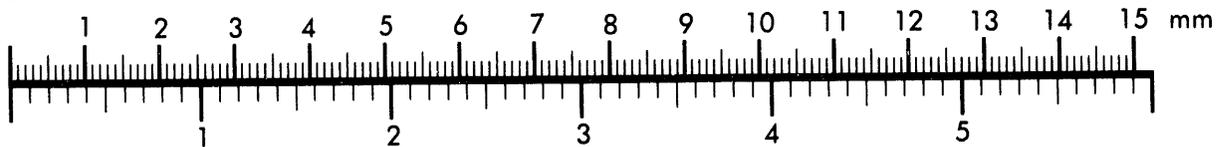
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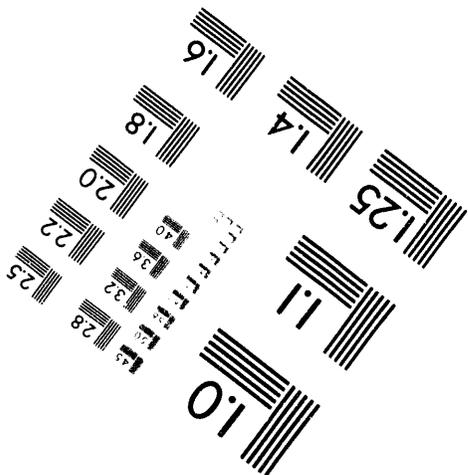1　2　3　4　5　6　7　8　9　10　11　12　13　14　15　mm

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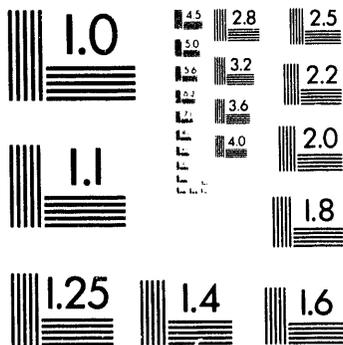
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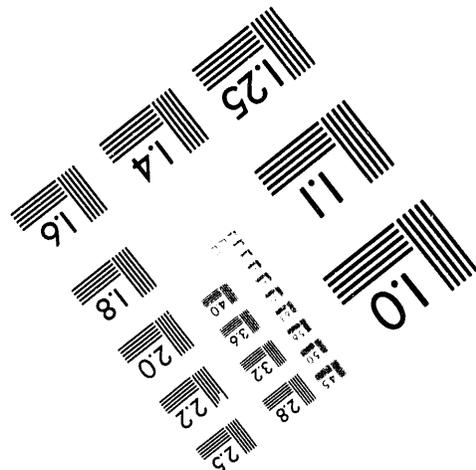
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HETEROGENEOUS NUCLEATION OF CALCIUM OXALATE ON NATIVE OXIDE SURFACES

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HETEROGENEOUS NUCLEATION OF CALCIUM OXALATE ON NATIVE OXIDE SURFACES

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ABSTRACT

The aqueous deposition of calcium oxalate onto colloidal oxides has been studied as a model system for understanding heterogeneous nucleation processes of importance in biomimetic synthesis of ceramic thin films. Calcium oxalate nucleation has been monitored by measuring induction times for nucleation using Constant Composition techniques and by measuring nucleation densities on extended oxide surfaces using an atomic force microscope. Results show that the dependence of calcium oxalate nucleation on solution supersaturation fits the functional form predicted by classical nucleation theories. Anionic surfaces appear to promote nucleation better than cationic surfaces, lowering the effective energy barrier to heterogeneous nucleation.

INTRODUCTION

Biomimetic synthesis of ceramic thin films involves crystal nucleation from supersaturated aqueous solutions onto substrate surfaces. Nucleation is stimulated using surface functional groups that mimic the role of active biomineralization proteins. The process can be used for low temperature deposition of oxides, hydroxides, sulfides, phosphates, and carbonates for applications ranging from producing hard coatings on plastics to producing biocompatible coatings for porous bone implants [1].

Classical theories [2] predict that the free energy for nucleation in biomimetic processing should depend on the level of solution supersaturation (S), the net interfacial energy for nucleation (σ), the temperature (T), and the particle surface area (A):

$$\Delta G = -RT \ln S + \sigma A \tag{1}$$

Critical parameters for film formation including the nucleation induction time (τ), nucleation density (N), and particle growth rate (dr/dt) are also controlled by S, σ, and T:

$$\ln (1/\tau) = \ln B - 16\pi\sigma^3 v^2/[3(kT)^3(\ln S)^2)] \tag{2}$$

$$\ln N = \ln P - Q\beta\sigma^3 v^2/[(kT)^3(\ln S)^2] \tag{3}$$

$$dr/dt = K(S-1)^n \tag{4}$$

where K, β, P, Q, B, and n are constants, k is Boltsmann's constant, and v is the molecular volume of the precipitating phase.

The key to successful biomimetic processing is to modify the substrate surface so that the net interfacial energy for nucleation on the surface is lower than the interfacial energy

associated with homogeneous nucleation and precipitation within the bulk solution. The purpose of this investigation is to use nucleation experiments to measure effective interfacial energies for both homogeneous and heterogeneous nucleation to try to determine factors that control interfacial energies. Once the factors that contribute to lowering the nucleation barrier are understood, it will be easier to modify substrate surfaces to promote film formation.

Calcium oxalate (CaOx) was selected as a model nucleating system because its solubility is well known [3] and is constant between pH 4 and pH 11. Supersaturation levels are relatively easy to control for CaOx over a wide range of solution conditions. The main substrates investigated include colloidal particles of the simple oxides silica, titania, and alumina. The above oxides each exhibit unique surface charge characteristics in the pH window of interest (Fig. 1) [4]. The surface charge can control the degree to which Ca^{2+} and Ox^{2-} ions are adsorbed or complexed in addition to controlling the contribution that the electrical double layer makes to the net interfacial energy. Each oxide also exhibits different lattice spacings and elastic constants. The interfacial strain energy for CaOx growing on each oxide is expected to be different, allowing investigation of the role of lattice mismatch in mediating surface nucleation.
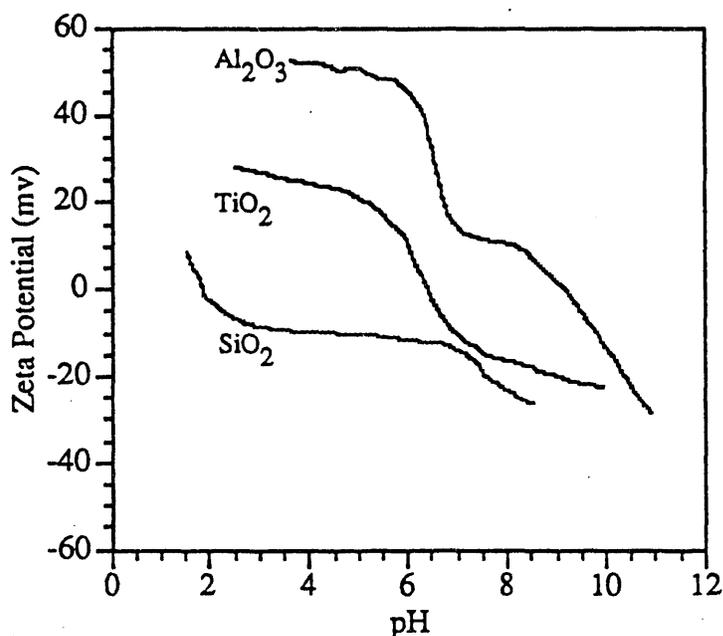

Figure 1. Zeta potentials of Al_2O_3, TiO_2 and SiO_2 (0.5v/v%) as a function of pH. T= 25°C, in 0.01M NaCl.

EXPERIMENTAL

The commercial powders α-Al_2O_3 (AKP-30, Sumitomo, surface area = 6.8 m²/gm), SiO_2 (PST-3, Nissan, 15 m²/gm), TiO_2 (P25, Degussa, 57 m²/gm) and $BaSO_4$ (Baker,6.8m²/gm) were used in Constant Composition (CC) experiments. Colloids were dispersed ultrasonically in 0.01 M NaCl solutions adjusted to the desired pH using HCl or NaOH and equilibrated for at least three days prior to CC experiments.

Stock solutions of calcium chloride and potassium oxalate were prepared from reagent grade chemicals (Fisher) using deionized, CO_2-free water and were passed through 0.2 μm Millipore filters before use. CC experiments were initiated by adding the desired colloidal slurry to freshly prepared supersaturated solutions containing equal Ca^{2+} and Ox^{2-}

2

concentrations. As Ca^{2+} was consumed by formation of CaOx, a calcium ion electrode commanded burettes to add Ca^{2+} and Ox^{2-} to the solution to keep solution supersaturation constant. Calcium consumption during CaOx formation was recorded with time to monitor nucleation induction times and crystal growth rates.

Nucleation densities were measured on single crystals of TiO_2 ((110) and (100) orientations, Princeton Scientific) exposed to supersaturated CaOx solutions. After immersion for fixed exposure times, samples were removed, rinsed with deionized water, and examined using a Nanoscope III atomic force microscope (Digital Instruments). The number density of CaOx crystals was determined by manual counting in several different fields of view.

RESULTS AND DISCUSSION

Bounding values for nucleation induction times are zero (for the case where CaOx seeds are used) and the time required for "spontaneous" nucleation that occurs on submicron particles of unknown origin that are always present in solution. Addition of colloids to solution can lead to induction times that are shorter than the spontaneous inductions times only when the added particles are more effective nucleation centers than the foreign particles that are already present. Depending on supersaturation levels, CC results (Fig. 2) show that addition of oxides can lower induction times for nucleation (obtained by extrapolating steady state slopes for Ca^{2+} consumption back to zero). For effective colloids such as silica, the difference between heterogeneous and homogeneous (spontaneous) induction times increases as S decreases. In all cases, the dependence of induction times with S fits the predictions of classical nucleation theory. A plot of $\log(1/\tau)$ vs. $(\log S)^{-2}$ yields a straight line (see Eq. 2) whose slope can be used to calculate σ (Fig. 3).

Figure 2. CaOx crystallization on different colloidal surfaces as a function of time at 25°C. $[Ca^{2+}]=[Ox^{2-}]=2.00\times10^{-4}$ M (S=3.3)

The σ values calculated from CC data are summarized in Table I, including literature data for CaOx formation on apatite [3]. The interfacial energy for truly homogeneous
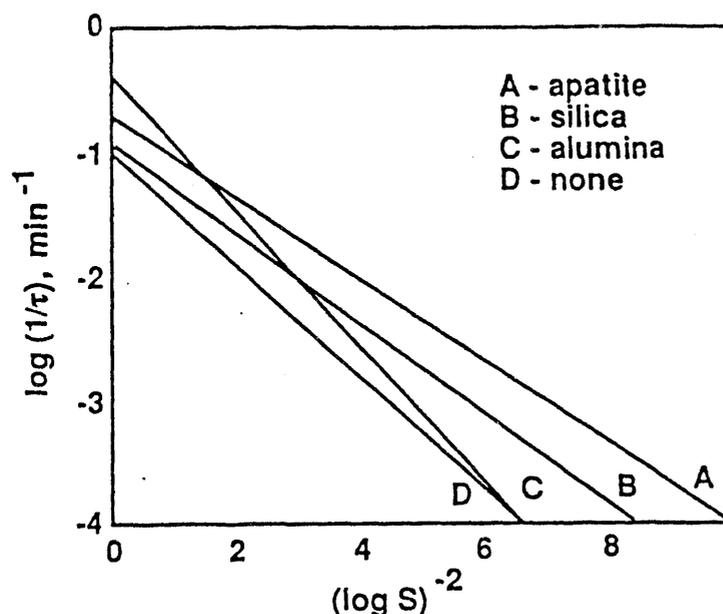
Figure 3. $\log(1/\tau)$ versus $(\log S)^{-2}$ for CaOx nucleation on apatite [3], SiO_2, Al_2O_3, and spontaneous nucleation.

Table I. Interfacial Energies (σ) of Various Surfaces Measured at 25°C. Ionic Strength = 0.01M NaCl.

Surface	$\sigma(mJ/m^2)$
homogeneous	69[1]
spontaneous (unseeded)	31
apatite	21[2]
$BaSO_4$	41
$Al_2O_3(+)$	37
$TiO_2(0)$	25
$SiO_2(-)$	24
$TiO_2(+)$	37
$TiO_2(0)$	25
$TiO_2(-)$	25

1. Reported in ref. [5].
2. Calculated from data in ref. [3].

nucleation is reported to be 69 mJ/m^2 [5]. The value of 31 mJ/m^2 obtained here for spontaneous nucleation agrees with the literature value [5]. Results for the intentionally added colloids fall into two groups: colloids that are less effective than the particles responsible for spontaneous nucleation (σ = 37-41 mJ/m^2), and colloids that appear to stimulate CaOx nucleation (σ = 21-25 mJ/m^2). For the case of TiO_2, the value of σ determined from AFM investigations of both (110) and (100) faces is in exact agreement with the value of σ calculated

from CC results (24 mJ/m^2).

The experimental values for interfacial energies can be used to examine trends and to establish whether observed changes in σ on different substrates are consistent with existing theories regarding interfacial energies. First, it appears that positively charge surfaces (TiO$_2$ at pH 5 and Al$_2$O$_3$ at pH 6.5, σ = 37 mJ/m^2) are not effective at nucleating CaOx, while neutral and negative oxide surfaces (TiO$_2$ at pH 6.5 and pH 8 and SiO$_2$ at pH 6.5) promote CaOx formation to an identical extent (σ = 24-25 mJ/m^2 for all three). As a further check of this observation, CaOx nucleation has been determined for Al$_2$O$_3$ at pH 6.5 having an adsorbed layer of the anionic surfactant dextran sulfate (Sigma). To date, the measured induction times are identical to those measured for silica at pH 6.5, indicating that the charge is indeed influencing nucleation times. The surface charge effect does not correspond to the change in interfacial energy predicted for the electrical double layer, because similar changes in interfacial energy result for both positive and negative surface charges. Instead, it appears that surfaces capable of adsorbing or complexing Ca^{2+} (including apatite) are more effective than surfaces having a higher affinity for Ox^{2-} when it comes to nucleating CaOx. Further experiments are planned to test this hypothesis.

The measured interfacial energies indicate that interfacial strain is not a major contributor controlling the nucleation process. The results are not consistent with a process that is controlled by epitaxial relationships between the nucleating crystal and the substrate. For the extended crystal-substrate interface, it is possible to estimate the interfacial strain energy based on the degree of lattice mismatch and the elastic constants of the crystal and the substrate [6]. Estimates for the strain energy range from around 40 mJ/m^2 for the CaOx:SiO$_2$ interface to around 120 mJ/m^2 for the CaOx:TiO$_2$ interface. Since the interfacial strain energies are large relative to the total interfacial energy for spontaneous nucleation, none of the colloidal oxides should be capable of nucleating CaOx if epitaxy is critical. The fact that different oxides having similar surface charges result in identical effective interfacial energies for CaOx nucleation reinforces this conclusion, as does the observation that nucleation on single crystal TiO$_2$ is insensitive to the orientation of the nucleating surface ((110) vs. (100)). Perhaps the insensitivity of the observed nucleation barrier to interface is due to the fact that the size of the critical nucleus is so small (a few ions for the range of S studied here) that adsorption by, rather than alignment with the lattice is most critical. The nucleus is so small that it can adapt to local bonding configurations rather than being forced to lattice match over an extended distance.

CONCLUSIONS

Nucleation of calcium oxalate from supersaturated aqueous solutions onto colloidal oxide particles is fit by classical nucleation theories. The dependence of both nucleation induction times and nucleation densities (on extended surfaces) fit theoretical predictions and can be used to extract experimental values for parameters such as the interfacial energy associated with nucleation. For CaOx, anionic and neutral colloidal surfaces appear to be more effective than cationic surfaces in promoting nucleation. Cationic surfaces can be activated to nucleate CaOx via adsorption of anionic surfactants. Contributions to the net interfacial energy to nucleation due to electrical double layers and interfacial strain appear to be less important than the ability of the surface to complex Ca^{2+}.

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