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Laser Induced Porosity and Crystallinity Modification of a Bioactive Glass Coating on Titanium Substrates

Functionally graded bioactive glass coatings on bioinert metallic substrates were produced by using continuous-wave (CW) laser irradiation. The aim is to achieve strong adhesion on the substrates and high bioactivity on the top surface of a coating material for load-bearing implants in biomedical applications. The morphology and microstructure of the bioactive glass from the laser coating process were investigated as functions of processing parameters. Laser sintering mechanisms were discussed with respect to the resulting morphology and microstructure. It has been shown that double layer laser coating results in a dense bond coat layer and a porous top coat layer with lower degree of crystallinity than an enameling coating sample. The dense bond coat strongly attached to the titanium substrate with a $10 \,\mu$ m wide mixed interfacial layer. A highly bioactive porous structure of the top coat layer. The numerical model developed in this work also allows for prediction of porosity and crystallinity in top coat layers of bioactive glass developed through laser induced sintering and crystallization. [DOI: 10.1115/1.4029566]

1 Introduction

Biomaterials are a class of materials used in biomedical applications for the repair and reconstruction of diseased or damaged parts of the human body. Their compositions can be categorized into four major classes: metals, ceramics, polymers, and composites. Based on their interaction with the human body, they can be classified into three additional groups: bioinert, bioactive, and bioresorbable [1]. Ti and its alloys, both bioinert metals, are most widely used in orthopedic implants due to their excellent bulk properties of high strength, ductility, corrosion resistance, and biocompatibility [2]. However, they do not provide strong enough bonding to bone due to interfacial stability problems with the host tissues [1,3,4]. Bioactive glasses, on the other hand, have the ability to form a HCA layer on their surface and in consequence naturally bond with bone. The rate of development of the interfacial bond between bioactive glasses and bone can be referred to as the level of bioactivity. Among the widely known bioactive materials hydroxyapatite (HA), 45S5 Bioglass, and A/W glass-ceramics, 45S5 Bioglass has the highest rate of bioactivity [5]. This leads to the rapid surface reactions that form a bone-bonding HCA laver [6].

The bonding between bioactive glasses and bone is biochemical bonding (i.e., ionic, hydrogen, etc.) [7]. However, the limited mechanical strength and low toughness of bioactive glasses prevented their use for load-bearing applications such as orthopedic implants [1,8]. In order to solve this issue, coating bioactive glasses onto biocompatible metal substrates has been developed. Among investigated coating methods such as enameling, plasma spraying, rapid immersion, pulsed laser deposition (PLD), electrophoretic deposition, ion beam sputtering, sol–gel technique and laser coating, enameling, and plasma spraying are the most commonly used coating methods. However, they presented cracks and porosity in the coating, caused relatively poor adhesion at the metal–glass interface, and high temperature treatments of the whole implant could damage the metal substrates [1]. On the other hand, laser coating is a localized heating process and has potential to both fusion bond and sinter the bioactive glasses on the metal substrates. Moritz et al. [9] explored the possibility of applying CO₂ laser irradiation for coating bioactive glass 1-98 on titanium medical implants. Mirhosseini et al. [10] used a combined laser/ sol-gel technique to produce calcium silicate coatings and determined its effect on osteoblast response. Cheng and Ye [11] investigated transmission laser coating of HA on Ti substrates. Comesaña et al. [12] investigated the potential of the laser cladding technique to produce S520 bioactive glass coatings on Ti6Al4V alloy substrates. Chen and Jia [13] made functionally graded composite material coatings of different HA and pure Ti mixture on Ti6Al4V alloy substrates by laser cladding. O'Flynn and Stanton [14] examined the effect of laser sintering on a G250 bioactive glass-ceramic, but their attempts to coat G520 on Ti6Al4V by laser enameling were unsuccessful. Studies referenced above reported laser coatings of different bioactive glass compositions. However, the laser coating of 45S5 Bioglass, which has the highest rate of bioactivity, has not been investigated yet. Furthermore, plasma spraying and enameling coatings are unsuccessfully performed for this material [15,16].

Among the factors that determine the effectiveness of a material as a bioactive agent are the textural and morphological properties. Three main factors that affect the bioactivity of bioactive materials are porosity, surface roughness, and crystallinity. Porosity of the implants greatly enhances their bone-bonding ability. Microroughening the bioactive glass surface significantly accelerated the early formation of surface reactions [17], and an increase in the surface area of the initial glass accelerates chemical reactivity in bioactive glasses. The crystallization rate of the apatite layer is affected by the texture of the silica substrate, increasing as pore size and pore volume increase [18-20]. Formation of silica rich and calcium phosphate-rich layers, indicating bioactivity, was slower on surfaces of samples that included sodium calcium silicate crystals than on the amorphous parent glass. The apatite formation increased from 10 hr for amorphous parent glass to 22-25 hr for 60-100% crystallized glass-ceramic [21]. Therefore, crystallization did not prevent the development of a crystalline HCA layer, but rather it increased the onset time of generating this layer. Effects of laser irradiation on microstructure and/or

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crystallinity of irradiated materials have been investigated such as laser induced poly(L-lactic acid) (PLLA) crystallinity reduction for degradation control in drug delivery application [22,23], and laser induced a-Si:H texturing and crystallization modification for overall stability enhancement in thin film solar cell applications [24]. However, laser induced Bioglass porosity and crystallinity modification for bioactivity improvement of surface-coated implants in biomedical applications has not been studied yet.

In this study, a Nd:YAG laser and a fiber laser both at 1064 nm wavelength are used to produce double layer coatings of 45S5 Bioglass on titanium substrates to achieve a functionally graded bioactive glass coating. This coating has a strong adhesion to the titanium substrates and high bioactivity on the top surface of the coating material. The sintering mechanisms, morphology, and microstructure of sintered bioactive glass, as well as the effects of laser processing parameters on the porosity and crystallinity of the coating material have been investigated. A numerical model is also developed to yield greater insight into the temperature dependent laser sintering behavior of the bioactive glass and to predict its porosity and crystallinity.

2 Background

2.1 Implants and Bioactive Glasses. Most implants, such as hip and knee replacements, which use only bioinert metal substrates, often suffer from problems of interfacial stability with host tissues. Bioactive glasses are a group of surface reactive biomaterials that have been used to repair and replace diseased or damaged bone in the human body. However, bioactive glasses alone are not strong enough to be used for these load-bearing applications. Therefore, applying a glass coating onto a mechanically tough substrate is an alternative to reduce the risk of early implant failure. Coating a substrate with a bioactive glass serves three purposes: The substrate is protected from corrosion, tissues are protected from corrosion products which may induce systemic effects, and the bioactive glass bond easily with bone. Bioactive glass coating of bioinert metal implants has increased bone-implant contact in the early growth period. Early bone ongrowth is known to increase primary implant fixation and reduce the risk of early implant failure. A common characteristic of bioactive glasses is a timedependent, kinetic surface modification that occurs upon implantation. When a bioactive glass is immersed in a physiological environment, such as a human body or simulated body fluid, reactions on the surface of this material are as following [8]:

(1) Ion exchange between modifier cations in the glass with ions in the solution leads to formation of silanols (Si-OH)

$$Si - O - Na^+ + H^+ + OH^- \rightarrow Si - OH + Na^+_{(solution)} + OH^-$$

(2) Hydrolysis, in which Si-O-Si bonds are broken and the glass network is disrupted, leads to further formation of silanols

$$2(Si-O-Si)+2(OH) \rightarrow Si-OH+OH-Si$$

(3) Polycondensation of silanols in which the disrupted glass network changes its morphology to form a hydrated silica gel-like surface layer

- (4) Precipitation, in which an amorphous calcium phosphate layer is deposited on the gel.
- (5) Mineralization, in which the calcium phosphate layer gradually transforms into a crystalline HA layer HCA.

When a layer of biologically active HCA forms, bonding of the implant with tissue can occur. The rate of HCA formation and the

031004-2 / Vol. 137, JUNE 2015

time for onset of crystallization varies greatly depending on the composition, morphology, and microstructure of the bioactive glass.

2.2 Kinetics of Sintering. Sintering is a processing technique used to produce density-controlled materials. Powdered particles join together by the application of thermal energy. Three categories of sintering processes are solid-state, liquid-phase, and viscous sintering. Densification of glass occurs by viscous flow, and viscous sintering is the dominant sintering mechanism for glasses. At temperatures above the glass transition temperature, glasses behave as ordinary Newtonian liquids. Due to surface tension, viscous flow takes place resulting in neck growth and shrinkage during sintering of glass particles. The work done by surface tension in decreasing the total surface area is equal to the total energy produced by dissipation of the flow of the viscous glass. Based on an energy balance concept, Frenkel [25] first proposed a viscous sintering, the neck growth and shrinkage are expressed as the follows:

$$x^2 = \frac{4\gamma_s a}{n}t\tag{1}$$

$$\frac{\Delta l}{l} = \frac{3\gamma_{\rm s}}{8\eta a}t\tag{2}$$

where *x* is the neck radius, *a* is the particle radius, γ_s is the surface energy, η is the viscosity, *t* is the sintering time, and $\Delta l/l$ is the shrinkage. The viscosity of glasses varies significantly from an average value of $10^{11.3}$ Pa · s at the glass transition temperature to a viscosity of ≤ 10 Pa · s at the practical melting temperature. The temperature dependence of the viscosity of glass is commonly expressed by the Vogel–Fulcher–Tamman (VFT) equation as follows:

$$\eta = \eta_0 \exp(\frac{B}{T - T_0}) \tag{3}$$

where η_0 is a constant, *B* is a variable related to the activation energy for viscous flow, T_0 is a fitting temperature ranging from zero to glass transition temperature, and *T* is the absolute temperature. When the glass powders are heat-treated over their transition temperature, a remarkable shrinkage of the material from viscous sintering occurs, and the powder structure starts consolidating and porosity is significantly reduced.

2.3 Kinetics of Crystallization. Both glass formation and crystallization are kinetic phenomena. The manufacture of glass is based on rapidly cooling the melt so that it will not form a crystalline, low-energy state [26]. Most glass-forming melts show some sign of crystallization if held just below the liquidus temperature long enough for structural arrangements to occur. Crystallization can occur either on cooling slowly from the melts or reheating to the temperatures below the melting point. The overall crystallization results from nucleation and crystal growth, and it could be analyzed using the Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory [27-29]. The primary crystalline phase in crystallization correlates strongly with the oxide content of the glass and its thermal history. In bioactive glasses, different crystal types can form depending on the composition. Bioactive glass 4585 has been reported to crystallize to Na2Ca2Si3O9 (2Na2O · CaO · 3SiO2) during heating [30,31].

The compositions of 45S5 bioactive glasses are in the $N_1C_2S_3-N_1C_1S_2$ composition region as shown in phase diagram of $CaO \cdot SiO_2-Na_2O \cdot SiO_2$ in Fig. 1 [32]. The crystals grown in this glass are solid solutions ($Na_2Ca_2Si_3O_9$ ss) having the chemical formula $Na_{4+2x}-Ca_{4-x}[Si_6O_{18}]$ ($0 \le x \le 1$). These solid solutions are formed by replacement of one Ca atom by two Na atoms. Ohsato et al. [33] explained that the structure of $Na_4Ca_4[Si_6O_{18}]$ in



Fig. 1 CaO SiO₂-Na₂O SiO₂ pseudobinary phase diagram of the sodium/calcium silicate system [32]

high temperature form, made up of puckered six-membered $[Si_6O_{18}]^{12}$ rings, is isostructural with Na₆Ca₃[Si₆O₁₈]. The structures consist of puckered six-membered rings of silicate tetrahedral, which are stacked in a cubic close-packing arrangement and held together by alkali and alkaline–earth ions. In the initial stage of phase transformation in both stoichiometric and nonstoichiometric glasses, the compositions of the crystals deviate considerably from those of the parent glasses [34]. The variation in the crystal composition is accounted for by the replacement of one Ca atom by two Na atoms. In the final stages of phase transformation, the average composition of crystals equals that of the parent glass. The crystals are solid solutions, and their composition changes during growth, approaching the parent glass composition with increasing crystal-lized volume fraction [35].

3 Numerical Simulation

Coupled modeling of the heat transfer, sintering potential, pore growth, and crystallization is performed to simulate the laser sintering behavior of bioactive glass. The laser radiation is considered as a heat source, and laser energy is assumed to be absorbed in a volume of a green body defined by a Gaussian distribution in the radial direction and exponential decay in the depth direction.

$$Q(r,z) = Q_0 \exp\left(\frac{-2r^2}{R_0^2}\right) \exp(-\alpha z)$$
(4)

where Q is the flux at point (r,z), Q_0 is the peak flux, R_0 is $1/e^2$ radius of the laser beam on the top surface, and α is the absorption coefficient of the green body.

In laser sintering, nucleation and crystal growth occur simultaneously, with rates that change continuously as the temperature changes during heating and cooling. According to the JMAK crystallization kinetics, the crystallized volume fraction for a nonisothermal condition can be expressed as [36]

$$X(T(t)) = 1 - \exp\left\{-\left(\int_{t_0}^t K(T(tt))dt'\right)^d\right\}$$
(5)

where X is the volume fraction transformed (crystallized), d is the dimensionality of growth (which is equal to 3 for homogeneous bulk crystallization), t is the time the sample experienced laser sintering, T is the temperature, and K is a temperature dependent crystallization rate that includes both nucleation and growth. Its function can be assumed by the Arrhenius equation

$$K(T) = K_0 \exp\left(-\frac{E_c}{RT}\right)$$
(6)

where E_c is the activation free energy of crystallization, R is the gas constant, K_0 is the pre-exponentials of crystallization rate, and T is the absolute temperature.

Based on the continuous media theory for selective laser sintering developed by Kolossov et al. [37], the porosity of the coating layer is defined by a sintering potential ϕ given by

$$\phi(T(t)) = 1 - \exp\left(-\int_0^t \zeta(T(\tau)d\tau\right)$$
(7)

where the range of ϕ is [0,1) corresponding to either the relative density of an original green body at $\phi = 0$ or fully dense glass $\phi = 1$. The rate of densification $\zeta(T)$ is first derived by Frenkel [25] and later expanded to be a temperature dependent function given by

$$\zeta(T) = \frac{\gamma(T)}{\eta(T)d_0} \tag{8}$$

where γ is the surface tension or surface energy, η is the viscosity of heat-treated material, and d_0 is a characteristic length scale of the initial material. The thermal conductivity of partially dense glass depends on the temperature and sintering potential, and is given by

$$k(\phi, T) = [a + (1 - a)\phi]k_{\text{bulk}}(T)$$
(9)

where k_{bulk} is the thermal conductivity of the bulk and *a* is the ratio between the conductivity of loose powder and the bulk conductivity. The temperature dependent viscosity of amorphous glass can be expressed using the VFT equation as mentioned in Sec. 2.2. When glass is partially crystallized, the effective viscosity, η_{eff} , will depend on the degree of crystallization and the viscosity of the amorphous glass. The effective viscosity can be approximated by the Einstein–Roscoe equation

$$\eta_{\rm eff}(X(T(t))) = \eta(T) \left(1 - \frac{X(T(t))}{X_{\rm max}}\right)^{-n} \tag{10}$$

where X_{max} and *n* are adjustable parameters, and the values of 0.75 and 2.5 are widely used, respectively [38]. When densification and crystallization take place simultaneously, the increase of effective viscosity may reduce the sintering rate and inhibit the densification. Only glass–glass contacts develop necks by viscous flow [39,40]; therefore, the modified sintering rate with concurrent crystallization could be expressed as

$$\zeta(T) = \frac{\gamma(T)}{d_0 \eta(T) \left(1 - \frac{X(T(t))}{0.75}\right)^{-2.5}} [1 - X(T(t))]$$
(11)

During the later stage of sintering, it is possible that an isolated pore containing gas may diffuse and coalesce with its neighboring pore. The rate of pore growth caused by pore diffusion and coalescence could be expressed as [41]

$$\frac{dr_{\rm p}}{dt} = \frac{mD_{\rm p}\gamma(T)\nu_{\rm p}}{r_{\rm p}^2k_{\rm B}T}$$
(12)

where r_p is a pore radius, *m* is a constant, v_p is the pore molar volume, k_B is the Boltzmann constant, and D_p is the pore diffusion coefficient, which is temperature dependent and can also be determined by the Arrhenius equation. The pore growth factor, P_g , can be calculated as a function of final pore radius, r_f , and initial pore radius, r_i

Journal of Manufacturing Science and Engineering



Fig. 2 Flow chart of the numerical model. It captures the combined effects of laser heating, densification, pore coalescence, and crystallization to predict degree of porosity and crystallinity.

$$P_{\rm g} = \frac{r_{\rm f}^3 - r_{\rm i}^3}{r_{\rm i}^3} \tag{13}$$

The overall porosity results from the competing mechanisms of viscous flow densification and pore coalescence. The overall porosity, *P*, can be determined as a function of initial density, ρ_i , sintering potential, and pore growth factor by the expression below

$$P = 1 - \{\rho_{\rm i} + (1 - \rho_{\rm i})\phi - P_{\rm g}[1 - \rho_{\rm i} - (1 - \rho_{\rm i})\phi]\}$$
(14)

To systematically predict temperature, sintering potential, pore growth, and crystallization, the mathematical model of each module described above needs to be rationally arranged. The flow chart of the integration of these modules is shown in Fig. 2. This



Fig. 3 Schematic representation of 45S5 Bioglass laser coating on a titanium substrate. Laser sintering of (a) the dense bond coat layer and (b) the porous top coat layer. The bond coat layer is necessary to achieve strong adhesion on the substrate. The top coat layer with a highly bioactive porous structure is beneficial for early formation of a bone-bonding HCA layer.

031004-4 / Vol. 137, JUNE 2015



Fig. 4 (a) Top-view optical micrograph and (b) cross-sectional SEM image of deposited glass powder layer by sedimentation; (c) image analysis to characterize porosity. The average porosity of deposited glass powder layer is 39.2%.

setup is solved using COMSOL MULTIPHYSICS. Simulation results offer a useful insight into the temperature dependent behavior of laser sintering, capturing the combined effects of laser heating, densification, pore coalescence, and crystallization on the result-ing porosity and crystallinity.



Fig. 5 (a) Top-view optical micrograph and (b) cross-sectional SEM image of the bond coat layer; (c) expanded view at the interface between Ti-substrate and the bond coat. Region at the center has a dense structure.



Fig. 6 (a) Cross-sectional SEM image of the interface region in Fig. 5(c) denoting a scanning area for (b) EDX composition map and a scanning line for (c) EDX composition profiles across the interface. It indicates titanium diffusion into the glass with a 10 μ m wide mixed interfacial layer.

4 Experimental Setup and Characterization

45S5 bioactive glass powder, obtained from Mo-Sci Health Care, was precoated on Titanium grade 2 substrates using a sedimentation method by mixing the glass powder with ethanol before depositing the glass slurry on the substrates. Before sedimentation, the substrate was ground using a 120 grit silicon carbide paper to roughen its surface, allowing for increased mechanical interlocking between the substrate and the coating layer. The sample is subsequently heated in a furnace at 120°C for 12 hr to assure that the ethanol is completely evaporated. A GSI Lomonics JK-2000 Nd: YAG laser and a SPI redEnergy G4 Fiber laser both operating in CW mode at a wavelength of 1064 nm were used for double layer coating of the bioactive glass on a titanium substrate. The Nd:YAG laser at fixed intensity of 40 W/mm² and scanning speed of 1.25 mm/s was used for coating the dense bond coat layer onto Ti substrates. A second layer of glass slurry was subsequently deposited on top of this densified bond coat. Finally, the fiber laser with spot size of $700 \,\mu\text{m}$ was used for sintering the porous top coat layer onto the dense bond coat layer of the bioactive glass. Laser powers of 10-12 W (intensities of 26-31 W/mm²) and scanning speeds of 1.0-2.0 mm/s were adjusted for sintering of the top coat. Laser coatings were performed with shielding by ultrahigh purity argon gas which was flowed on the surface at a flow rate of 12 scfh. A schematic diagram of the experimental setup is illustrated in Fig. 3.

The glass powder is highly transmitting at the 1064 nm wavelength; however, due to multiple surface scattering [42], the overall absorptivity of deposited glass powder is as high as the case of a nonlinear absorption mechanism [43] after measuring the timeaveraged laser power that passes through the deposited glass powder layer on fused silica. After laser coating, the samples were embedded in epoxy molds, and then ground with silicon carbide papers and polished with alumina and leather polishing pads to examine the cross section views using a Hitachi S-4700 scanning electron microscope (SEM). Compositional analysis was also performed using energy dispersive X-ray spectroscopy (EDX) on the Hitachi S-4700. Morphology and microstructure of the bioactive glass were also observed using an Olympus BX-60 optical microscope. An Inel XRG-3000 X-ray diffractometer (XRD) with CuK α radiation was used to determine the crystallization phase and percent crystallinity.

5 Results and Discussion

5.1 Morphology and Porosity of Pretreated Glass Powder. For 45S5 Bioglass, which has the highest rate of bioactivity, coatings by plasma spraying or enameling usually fail due to the lack

Journal of Manufacturing Science and Engineering



Fig. 7 Cross-sectional SEM images of (a) direct laser sintering (from the denoted rectangular area in Fig. 5(b)) of a porous glass layer onto a Ti-substrate; (b) a second layer of glass powder deposited on the dense bond coat before another laser irradiation; (c) morphology of resulting dense bond and porous top coat layers by laser coating; (d) the fluorescence micrograph of pores opened to the top surface. Figure 7(a) shows weak attachment of porous glass coating directly on a titanium substrate as compared to the double layer coating with a dense structure having strong adhesion on the substrate and with a highly bioactive porous structure on the top surface in Fig. 7(c).

of adhesion to the substrate [15,16]. By properly controlling the parameters of laser irradiation on the glass powder layer, a functionally graded 45S5 Bioglass coating with dense structure having strong adhesion on a titanium substrate, and with a highly bioactive porous structure on the top surface was achieved. Figures 4(a)and 4(b) show the representative top-view optical micrograph and cross-sectional SEM image of this deposited powder layer before laser irradiation. The crushed 45S5 Bioglass powder has no specific shape, with particle size $<50 \,\mu\text{m}$. These glass particles temporarily stay together to form a thin layer on the titanium substrate. The deposited powder layer has high porosity as shown in Fig. 4(b). The porosity was characterized using image-analysis by direct observation of the cross sections of the deposited powder layer. Areas of the glass particles and the pores were separately specified as shown in Fig. 4(c). Boundary lines of glass particles were specified, and area fraction calculation of porosity was done by using IMAGEJ software. The average porosity is 39.2%, or the relative density of the deposited glass powder layer is 60.8%.

5.2 Bond Coat Layer on the Ti Substrate. The coating of a bioactive material on a bioinert metal for orthopedic implants is considered to be successful if the coated material is strongly adhered onto the substrate. Laser irradiation of the glass particles increases their temperature such that the viscosity of 45S5

Bioglass is decreased from the softening point $(10^{6.65} \text{Pa} \cdot \text{s})$ to the practical melting point $(10 \text{ Pa} \cdot \text{s})$. For the required dense structure of the bond coat layer, higher laser power for increasing the temperature of 45S5 Bioglass above its practical melting point is required. Figure 5 shows the morphology of this desired bond coat layer in both top and cross section views. Due to the Gaussian distribution of the laser beam, there are two distinctive regions of laser affected zone as shown in the top-view optical micrograph in Fig. 5(a). The dark center region apparently has a dense structure, and the glass powder is believed to reach the melting temperature in this area. With lower laser intensity in the peripheral area of the beam, the resulting gray region has a porous structure. The glass powder experiences temperatures above the softening point and sintering takes place in this area. There is a transition between these two regions, and the microstructure in the transition area will be discussed in Sec. 5.3.2. From the cross-sectional view in Figs. 5(b), and 5(c), it indeed shows that the center region has a dense structure, and there is continuity without any lateral cracks on the coating interface between the 45S5 Bioglass and the titanium substrate. On the other hand, there is a distinctive gap between the deposited powder layer and the substrate as shown in Fig. 4(b). Figure 6 shows an EDX composition map and line scan composition profiles across the interface as depicted in Fig. 5(c). The existence of a $10 \,\mu m$ wide mixed interfacial layer is clearly shown in Figs. 6(a) and 6(c). In a thermally activated process,

031004-6 / Vol. 137, JUNE 2015

there is diffusion of titanium into silicate glass melts [44,45]. When the thermal energy of a titanium atom is greater than its activation energy, it could break interatomic bonds to move into melted glass causing interfacial reactions to form titanium silicides and titanium oxide [46,47]. The EDX composition map in Fig. 6(b) shows that Ti from the titanium substrate diffuses toward the glass, resulting in relatively strong chemical bonding so the bond coat layer could not be manually removed from the titanium substrate.

5.3 Top Coat Layer on the Bond Coat

5.3.1 Morphology and Porosity. The porous structure on the top surface of the coated implants is desirable for high bioactivity. It can be achieved by applying lower laser powers to not reach the melting regime of the 45S5 Bioglass, but high enough to induce sintering of the material. If the processing parameters are used for coating the porous top coat layer directly onto the titanium substrate, there will be a gap between the bioactive glass and the substrate as shown in Fig. 7(a), and the coating layer would be easily detached from substrate by applying a relatively small force. Therefore, the bond coat layer of bioactive glass as discussed in Sec. 5.2 is essential. The deposition of the 45S5 Bioglass powder on the bond coat layer is shown in Fig. 7(b). This deposited glass powder layer was laser irradiated under sintering conditions resulting in the top coat layer as shown in Fig. 7(c). The glass powder was successfully sintered together and also bonded with the bond coat layer. It is clear that the top coat layer has a porous structure with mostly closed pores, but some open pores are found near the top surface. The fluorescence micrograph in Fig. 7(d)shows the existence of the open pores as a fluorescent dye mixed with epoxy flows into those pores from the top surface. Since the 45S5 Bioglass is originally an amorphous material, the dominant material transport mechanism is the viscous flow. The densification by viscous flow proceeds more rapidly than that by other solid-state diffusion mechanisms [48,49]. During laser sintering, the decrease in temperature-dependent viscosity causes the orientation of glass particles to be changed, and glass particles will develop more points of contact. Neck formation at the contact points and neck growth subsequently occur together with the formation of an array of interconnected pores. Finally, the shape and



Fig. 8 Cross-sectional SEM images of (a) double layer laser coating; (b) expanded view at the porous top coat layer; and (c) the pre-existing interface between two layers. Swelling of the porous top coat layer results from pore coalescence dominating over viscous flow densification. There is no gap between the bond and top coat layers.

size of particles and pores gradually change until the pores become isolated. Figure 8 shows the SEM cross section micrographs with expanded views of isolated pores and pre-existing interface area between the two glass layers. There is no distinctive gap between the layers as shown in Fig. 8(c). With the open pore structure of the deposited glass powder layer as seen in Fig. 7(b), the sintering atmosphere has important effects on densification and microstructural development during sintering. Atmospheric gas will get trapped inside when the pores pinch off and become isolated. For an insoluble gas like air, the gas is compressed and its pressure increases as the shrinkage of the isolated pores takes place. When the gas pressure becomes equal to the driving force for sintering, the shrinkage stops. At the same time, it is possible that diffusion of the gas between neighboring pores can occur [50]. Temperature gradients and gas pressure differences in various sizes of pores are the driving force for the diffusion. Volume shrinkage due to densification by viscous flow and volume expansion due to pore growth (or pore coalescence) by gas diffusion



Fig. 9 (a) Optical micrograph of crystallized 45S5 bulk glass heat-treated in the furnace; (b) top-view optical micrograph (expanded view from the denoted rectangular area in Fig. 5(a)); and (c) top-view SEM image of the partially crystallized dense area by laser sintering; (d) EDX composition profiles show that crystals are calcium-rich compared to the amorphous glass

Journal of Manufacturing Science and Engineering



Fig. 10 XRD spectra of (a) the enameling process sample fired at 750 °C for 15 min in the furnace, (b) laser sintering of the porous top coat layer at 12 W and 2.0 mm/s, and (c) amorphous 45S5 bioactive glass powder deposited by sedimentation. Laser sintering causes less crystallinity than enameling, which is beneficial for bioactivity of implants.

will compete with each other. When the pore coalescence is more dominant than viscous flow densification, swelling of the laser sintering region occurs as shown in Fig. 8(*a*). Since laser sintering is a considerably fast heating and cooling process, most of the pores do not have enough time to rise to the surface based on their buoyancy. Different spherical-like shapes of various pores, resulting from the competition between viscous flow densification and pore coalescence is shown in Fig. 8(*b*). They range from 6 to 10 μ m. The overall porosity of laser sintering of 45S5 Bioglass depends on not only viscous flow densification and pore coalescence but also crystallization which will be discussed in Sec. 5.3.2.

5.3.2 Microstructure and Crystallinity. Thermal treatments of 45S5 Bioglass above the glass transition temperature lead to crystallization. Crystallized or devitrified glass occurs by nucleation of the crystal phase and subsequent growth. A bulk 45S5 Bioglass sample can be fully crystallized, and the microstructure of heattreated bulk 45S5 Bioglass is shown in Fig. 9(a). From this optical micrograph, the grain structure and boundaries are clearly observed, and the average grain size is roughly ten microns. For 45S5 Bioglass powder, during heat treatment, sintering and crystallization occur at the same time. In the sintering temperature range, a material experiences necking and becomes denser due to viscous flow. At the same time, it also starts nucleation and growth of the Na₂Ca₂Si₃O₉ crystal phase, and the material will be partially crystallized. With laser irradiation, the heating and cooling times are so fast that the result of treated glass powder will be either fully dense glass without a crystal phase or porous glass with a partially crystallized phase. This depends on whether or not the treatment temperature is above the melting point. In this study, a higher laser power condition was selected to induce melting of the glass powder so that it would fusion bond with the titanium substrate, resulting in a strong adhesion to the substrate as shown in Fig. 5(a). However, in the peripheral area of the Gaussian laser beam, there is a sintering region. From the left to the right of the indicated area in Fig. 5(a), there are sintering, transition, and melting regions, respectively, as shown in Fig. 9(b). Among these regions, glass powder experiences different temperature regimes. On the left hand side, the temperature is within sintering temperature but lower than melting point; therefore, it becomes partially crystallized and porous glass. On the right hand side, the temperature is above the melting point; therefore, it becomes densely amorphous glass. However, in the transition region, there is



Fig. 11 (a) Porosity and (b) crystallinity of laser sintering samples versus laser scanning speed. Error bars denote standard deviation. Faster scanning speeds correspond to the formation of higher porosity and lower crystallinity.

partially crystallized dense glass with cubic like isolated grain approximately five microns in size. In this region the temperature is supposedly high enough to fully densify the residual glass and the Na₂Ca₂Si₃O₉ crystal phase together, but lower than the liquidus temperature of the crystal phase. Figure 9(d) shows line scan EDX composition profiles across the two isolated crystals in Fig. 9(c). Based on the phase diagram of the CaO \cdot SiO₂ - Na₂O \cdot SiO₂ in Fig. 1, even though there is a continuous variation in glass and crystal compositions during crystallization by the replacement of one Ca atom by two Na atoms in the crystals [33,35], the crystals should be calcium-rich and sodium-depleted when compared to the parent glass as shown in Fig. 9(d). Figure 10 shows the XRD spectra from the deposited glass powder layer by sedimentation, the laser coating sample, and the coating sample by enameling. The deposited glass powder shows a typical amorphous spectrum with single broad peak. In both partially crystalline samples, the diffraction pattern and all distinctive peaks agreed with those of the Na₂Ca₂Si₃O₉ crystal phase reported on portable document format (PDF) card No. 04-011-6167. The spectrum of the enameled sample by firing in the furnace at 750 °C for 15 min shows higher peak intensity than the laser coating sample, and it shows that the crystallinity of the laser coating sample is lower than the enameling coating sample. The lower degree of crystallinity is more



Fig. 12 (a) Porosity and (b) crystallinity of laser sintering samples versus laser power. Error bars denote standard deviation. Crystallinity is more-or-less constant with laser powers.

desirable for achieving the high bioactivity of the implants. The quantification of crystallinity and porosity of laser coating samples at different processing parameters were performed and discussed in Sec. 5.3.3.

5.3.3 Effect of Laser Processing Parameters. The overall porosity of a laser coating sample was characterized by using image-analysis to directly observe a sintering cross-sectional area of the porous top coat layer of bioactive glass. The boundary line of the sintering area was traced, and its area was calculated and compared with the powder-deposited area before laser sintering to determine the overall porosity. The degree of crystallinity of a laser sintering sample was quantified by comparing its integrated peaks intensity in XRD spectrum to that of the fully crystallized sample [51]. A heat-treated sample at 750 °C in the furnace for 10 hr is assumed to be fully crystallized and its spectrum was used as a reference. Figures 11(a) and 11(b) show the porosity and crystallinity of laser sintering samples as a function of laser scanning speed. Both of these quantities are strongly dependent on the scanning speed. Faster scanning speeds correspond to the formation of higher porosity where pore growth becomes more dominant as compared to densification. This implies that sintering time has more influence on the viscous flow densification than the pore growth. However, at the highest power of 12 W and the lowest

scanning speed of 1.0 mm/s, the overall porosity is less than the deposited glass powder layer as shown in Fig. 11(a). The higher sintering temperature (close to the melting point) and the longer sintering time made the viscous flow densification dominant. Figure 11(b) shows that sintering time significantly influences the crystallization kinetics. Longer sintering times result in larger crystal fraction of the laser sintering sample. The porosity and crystallinity of laser sintering samples as a function of laser power are shown in Figs. 12(a) and 12(b). For higher laser powers, the pore growth further dominates the densification at the scanning speed of 2.0 mm/s. This implies that the sintering temperature has more influence on the pore growth than the sintering time does. However, at the scanning speed of 1.0 mm/s, the higher laser powers induced higher sintering temperature (close to the melting point) resulting in the transition for the dominant mechanism from the pore growth to viscous flow densification, as shown in Fig. 12(a). At the same scanning speeds, the crystallinity is more-orless constant with the laser power as shown in Fig. 12(b). Since the crystallization temperature of 45S5 Bioglass is below 750°C [52], the increase in sintering temperature far beyond this temperature by higher laser power has little effect on the crystallinity. All processing conditions result in a porous structure with low crystallinity; therefore, the laser coating is a viable process for bioactive glass coating of biomedical implants.

5.4 Numerical Modeling. 2D axisymmetric finite element method laser sintering models with the set of coupled heat transfer, crystallization, sintering, and pore coalescence equations, solved concurrently within a spatially resolved finite element domain, are implemented to simulate the porosity and crystallinity of the laser sintering layer. Since a laser beam is stationary on a single spot in these 2D axisymmetric numerical models, they will be validated using experimental results at different laser powers by assuming that the laser irradiation times are approximately equal to the division of a laser spot size (0.7 mm) and laser scanning speeds. Figure 13 shows a representative 2D revolution (225 deg) of temperature distribution of the laser sintering from the numerical simulation. Peak temperature is below the apparent melting point of 45S5 Bioglass. However, it is high enough to sinter the glass powder onto the bond coat layer, resulting in the porous top coat layer. Figure 14 shows cross-sectional views of the crystallinity, sintering potential, and porosity from the numerical simulation, as well as an experimental feature for comparison. The size of the sintered and crystallized area of bioactive glass in the model as shown in Figs. 14(a)and 14(b) is essentially comparable to the experimental sintered area in Fig. 14(d). The resulting porosity in the model as shown in Fig. 14(c) is calculated from the combined effect of densification and pore growth using Eq. (14). The porosity contour map in Fig. 14(c) corresponds well with the morphology of the sintered glass in Fig. 14(d). Compared to the initial porosity of deposited glass powder, the porosity of the sintered glass is higher at the center of the laser-irradiated area while lower at the peripheral area, because pore growth is dominant compared to densification at higher temperatures. To validate the numerical models with the experimental results, the overall porosity of sintered glass in the models for each processing condition is determined from the average of spatial porosity within the sintering region. Additionally, the crystallinity is determined from the average of spatial crystallinity within sintered radius in the r-direction and the X-ray penetration depth in zdirection. For the XRD equipment used in this study with 25 deg incident angle, the X-ray penetration depth is 57.98 μ m. Figure 15 shows the numerical and experimental results of porosity and crystallinity as a function of laser power. The numerical results correspond well with the experimental results by predicting an increasing trend of the porosity and a more-or-less constant trend of the crystallinity with the laser power. At the same scanning speed, the increasing porosity shows that the higher temperature distribution from the higher power condition results in more driving force for gas entrapped in the pores to diffuse and coalesce with the

Journal of Manufacturing Science and Engineering



Fig. 13 Representative revolution (225 deg) of 2D temperature distribution of a coupled lasersource heat transfer, sintering potential, pore growth, and crystallization model (laser power of 11 W, at 0.35 s of laser irradiation)

surrounding ones, and the pore growth mechanism further dominates the densification. On the other hand, temperatures much higher than the onset temperature of crystallization mentioned in Sec. 5.3.2 have less effect on the crystallization kinetics compared to crystallization time. Therefore, the crystallinity of sintered glass is nearly constant with the laser power. The porosity predicted from numerical models may have a small discrepancy compared with that from the experimental results; however, the numerical model is proved to predict the right trends and yield greater insight into the temperature dependent behavior of laser sintering of glass.



Fig. 14 2D cross-sectional images for (a) crystallinity, (b) sintering potential, and (c) porosity; (d) the morphology of sintered glass in comparison to the numerical porosity (at same laser power of 11 W, numerical irradiation time of 0.35 s, and experimental scanning speed of 2 mm/s)

031004-10 / Vol. 137, JUNE 2015



Fig. 15 Numerical (dashed lines) and experimental (solid lines) percentages of porosity and crystallinity at different laser powers (at 0.35 s of numerical laser irradiation time and at 2 mm/s of experimental scanning speed). Numerical models predict an increasing trend of porosity and more-or-less constant trend of crystallinity with the laser powers.

6 Conclusion

Laser coating of 45S5 bioactive glass on titanium substrates has been investigated for biomedical implants. Line scan EDX composition profiles show that there is mixed interfacial layer between a dense bond coat layer and the titanium substrate indicating a relatively strong chemical bonding. A porous top coat layer is successfully sintered onto the bond coat layer with no interface. All processing parameters investigated here for the top coat layer result in a porous structure with low crystallinity. The overall porosity of laser coating results from competing mechanisms between viscous flow densification and pore coalescence. Swelling of the porous top coat layer is due to pore coalescence dominating over viscous flow densification. Higher porosity and lower crystallinity correspond to faster scanning speeds while crystallinity is more-or-less constant with laser powers. The numerical models developed in this work aid in understanding the laser sintering mechanisms and allow for prediction of the overall porosity and crystallinity in top coat layers. The numerical results correspond well with the experimental ones. The work described above shows that double layer laser coating of the 45S5 bioactive glass with high level of bioactivity is successfully done.

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