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Metalorganic solution deposition of lead zirconate titanate films onto an additively manufactured Ni-based superalloy

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ABSTRACT

Recent advances in additive manufacturing of high-temperature alloys for structural aerospace applications has led to interest in integrating additional functionality into such parts. Lead zirconate titanate (PZT) is a prototypical ferroelectric ceramic used as the electro-active material in many piezoelectric sensors and actuators. In this study, 300 nm thick $PbZr_{0.2}Ti_{0.8}O_3$ (PZT 20/80) films were grown using metalorganic solution deposition onto additively manufactured substrates of Inconel 718. The microstructures of the films and the nature of the film/substrate interfaces were characterized using a combination of X-ray diffraction and electron microscopy techniques. Electrical measurements were performed to determine the ferroelectric, dielectric, and conductive responses of the PZT films. Our findings show that the PZT films exhibit robust ferroelectricity characterized by well-defined polarization-applied electric field (*P*-*E*) hysteresis loops. The samples display internal bias of up to ~40 kV/cm. The room temperature remnant polarization and the small signal dielectric permittivity are ~70 $\mu C/cm^2$ and 205, respectively. The dielectric loss (tan δ) and the leakage current at 1 kHz are 9% and 1 nA at 1 V, respectively. We attribute the internal bias observed in the hysteresis loops and the overall large dielectric losses to the presence of an intermediate oxide layer at the PZT/Inconel interface, which forms during the high temperature crystallization of the ferroelectric film. These results show that it is possible to grow functional oxides with promising electrical properties onto additively manufactured metallic substrates.

1. Introduction

Additive manufacturing currently spearheads a renewed focus on the manufacturing sector in most industrialized countries. Since additive manufacturing does not require tooling, development times for components can be reduced, and low volume parts might be produced at a cost advantage compared to traditional manufacturing techniques. Additive manufacturing uses metal powders, thereby reducing the amounts of scrap metal generated as compared with traditional manufacturing approaches, while offering new design opportunities. Additive manufacturing arguably draws the greatest attention when considering the potential to re-design components under the umbrella of topology optimization. The perceived advantages of additive manufacturing over conventional manufacturing, along with major research and development investments, put pressure on accelerating the insertion of additive manufacturing into the production environment. Hence, it is not surprising that most additive manufacturing development programs within the aerospace realm have initially focused on existing aerospace alloys such as Ti-6Al-4V and Inconel 718 [1,2].

The additive manufacturing community has pursued Inconel 718 mainly because of the widespread use of this alloy for aerospace applications, and in particular for jet engine components. About one-third of a typical aircraft jet engine is made from Inconel

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718, and this material is used for critical rotating parts, airfoils, or supporting structures [3,4]. The extensive use of this alloy derives mainly from a balanced combination of properties such as tensile, fatigue, creep, and rupture strengths, along with reasonable cost and ease of fabrication [5–7]. Inconel 718 belongs to the family of Ni-based superalloys, and true to the nature of this material group, comprises several alloying elements, each with a specific function [8].

The processing-microstructure-property trinity for Inconel 718 has been assessed for traditional manufacturing techniques such as castings and forgings since the 1950s, generating an extensive body of research results. The recent meteoric rise of additive manufacturing prompted several studies of processing-microstructure-properties relations for additively manufactured Inconel 718 over a short time [9–11]. These publications have almost exclusively focused on structural applications. However, the layer-by-layer processing technology should offer the much sought-after ability to integrate functional elements such as sensors and actuators into structural components [12]. The development of hybrid components with functional and structural elements faces several challenges and raises fundamental materials questions. One of the most critical aspects is the behavior of the functional material component when combined with additively manufactured alloys. The combination of ferroelectric oxides with aerospace alloys, such as Inconel 718 as a base metal substrate, serves as a paradigm in this work for hybrid structural/functional components. While processing challenges such as lattice mismatch, disparity in coefficients of thermal expansion (CTE) between films and substrates, and diffusion of elemental constituents during crystallization can result in potential limitations for the functional behavior, there have been some reports of successes in depositing ferroelectric oxides on metal-based bottom electrodes like nickel, steel, and Inconel [13,14].

Among the most widely used ferroelectric oxides and hence the functional component of choice for this study is lead zirconate titanate [$PbZr_xTi_{1-x}O_3$, PZTx/(1-x)]. PZT is a ferroelectric, piezoelectric and pyroelectric solid solution, which has found applications in sensors, actuators, and memory devices [15–17]. PZT thin films can be grown using a variety of methods including pulsed laser deposition (PLD) [18,19], molecular beam epitaxy (MBE) [20], and metal-organic chemical vapor deposition (MOCVD) [21]. These techniques produce high-quality films with uniform thickness and precise compositional control, but are relatively expensive [14]. Therefore, more cost-effective methods such as chemical solution deposition (CSD) and its variations, including sol-gel and metal-organic solution deposition (MOSD), are considered. Such techniques provide good compositional control and uniformity over large areas. Nickel [17,22–27] and Ni-based alloys including NiCrAlY [28], Invar [29], Hastelloy [30], and Inconel 750 [31–33] have been explored as substrates for PZT. There are two main problems that hamper further development. Firstly, the significant mismatch in the coefficient of thermal expansion (CTE) between PZT and Inconel ($11 \times 10^{-6}\,^{\circ}C^{-1}$ for PZT [34]*vs.* ~$13 \times 10^{-6}\,^{\circ}C^{-1}$ for Ni) results in thermal stresses that may cause spallation, delamination, and cracking, since typical ferroelectrics and other functional ceramics are mostly crystallized at fairly high temperatures (mainly $T > 600\,^{\circ}C$). The CTE mismatch may also reduce dielectric and piezoelectric properties [35]. Secondly, it can be expected that oxidation of Ni and its alloys at high processing temperatures, along with inter-diffusion between substrate and functional film [36], might result in degradation of ferroelectric, dielectric, and piezoelectric properties.

A typical method to overcome CTE and diffusive problems is to deposit an appropriate metal oxide buffer layer, e.g., $SrTiO_3$, PbO, yttria-stabilized zirconia (YSZ), $YBa_2Cu_3O_7$ (YBCO), $SrRuO_3$, RuO_2, or $La_{1-x}Sr_xCoO_3$ (LSCO) [14]. For example, 2 μm thick PZT 52/48 films grown on Ni foils with HfO_2 buffer layers reveal remnant polarization, dielectric permittivity and loss tangents of 36 $\mu C/cm^2$, 780 and 4%, respectively [27]. PZT 52/48 films have also been grown on Inconel 750 using a $La_{0.8}Sr_{0.2}MnO_3$ (LSMO) buffer layer via a sol-gel method with good dielectric properties [32]. Remnant polarization, relative permittivity and dielectric loss of 25 $\mu C/cm^2$, 800 and 10%, respectively, have been reported for 3 μm thick PZT films on 200 nm thick LSMO buffer layers with Inconel 750 substrates. Buffer layers add manufacturing complexity, which can result in reduced properties of the overall material stack and should therefore be avoided, if at all possible. What is essentially needed is the development of processing protocols that allow for functional ceramics to be deposited directly onto metals. The objective of this study is therefore to test the hypothesis that ferroelectric behavior can be obtained from PZT films that are grown directly onto additively manufactured Inconel 718 substrates using a simple solution deposition technique. This study should be seen in the context of demonstrating feasibility rather than demonstrating an advanced technology readiness level.

2. Experimental methods

AM Inconel 718 substrates were fabricated with an EOS 270 Direct Metal Laser-Sintering (DMLS) machine. The Inconel 718 substrates were ground and polished using standard metallurgical techniques in order to improve the surface roughness for the deposition of ferroelectric films. The average surface roughness (R_a) of the bare substrates was determined to be 23 nm, using a Zygo NewView 7000 profilometer.

$Pb_{1.1}Zr_{0.2}Ti_{0.8}O_3$ precursor solution was used to directly deposit PZT 20/80 thin films onto the Inconel 718 substrate via CSD. PZT 20/80 was chosen due to its tetragonal crystal structure in the ferroelectric state that simplifies the structural analysis in this work. Stoichiometric portions of zirconium (IV) tert-butoxide, titanium (IV) isopropoixde, and lead (II) acetate trihydrate (10% excess lead) were added to acetic acid, and 2-methoxymethanol to make a 0.2 M PZT 20/80 precursor following a route described in Ref. [37]. The PZT solution was deposited onto the substrate through a 0.2 μm filtered syringe and spun at 4000 rpm for 50 s using a Laurell spin coater. After deposition of the first layer, the substrate was dried on a hot plate at 200 °C for 30 s, followed by pyrolysis at 300 °C for 5 min, and annealing at 700 °C for 1 min in separate furnaces in air. For subsequent layers, drying was performed for each layer. Once a total of 8 layers were deposited, the stack was pyrolyzed for an additional 15 min and annealed for 10 min at 700 °C, resulting in an overall film thickness of ~300 nm. Further details of the film deposition process can be found in literature [38].

X-ray diffraction (XRD) studies were carried out using a Bruker D5005 diffractometer with a Cu K_{α} source to determine the crystallographic phases present and degree of crystallinity. PZT 20/80 powder was examined using the Bragg-Brentano configuration, whereas grazing incidence diffraction at a 5° incident angle was used for the bare substrates and substrates coated with PZT films. The latter arrangement was employed to decrease the depth of X-ray penetration and thus, to limit intensities of peaks from the Inconel substrate in the patterns from the PZT thin films.

Microstructural data was obtained using a combination of dual-beam focused ion beam scanning electron microscopy (FIB-SEM), and scanning transmission electron microscopy (STEM) techniques. PZT 20/80 film surface was examined using the electron column in an FEI Helios Nanolab 460 FIB-SEM. Cross-sectional TEM samples of the coating and substrate were then prepared by first depositing Pt *in-situ* to protect the region of interest during Ga^+ ion milling, cutting parallel trenches to define a pre-thinned lamella, and then