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Fabrication and post heat treatment of $0.5Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.5Pb(Zr_{0.48}Ti_{0.52})O_3$ coatings by supersonic plasma spray

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ABSTRACT

$Pb(Mg_{1/3}Nb_{2/3})O_3$-$Pb(Z_{r0.48}Ti_{0.52})O_3$ coatings were obtained by supersonic plasma spray. With subsequent heat treatment, compact structure and typical tetragonal phase were obtained, and therefore dielectric performance ($\varepsilon_r \approx 915$ at ambient temperature) have been significantly improved. The reason for successfully promote the properties is attributed the elimination of defects, amorphous and pyrochlore phase. Detail analyses were conducted on the variation of defects (pores and micro-cracks) and phase (amorphous, pyrochlore) of coatings after treated at elevated temperature. With the analyses, the existence of pyrochlore phase and ZrO_2 are attributed to the incongruent melting behavior. Inhibition of grain growth is attributed to the accumulation of ZrO_2 in the grain boundary. The results also suggest the subsequent change from pseudocubic to tetragonal at elevated temperature.

1. Introduction

Lead-based relaxors with excellent electromechanical performance ferroelectric ceramic have attracted many attentions on the application of multilayer ceramic capacitor, actuator and transducer [1–3]. Lead zriconate tianate (PZT) and lead magnesium niobate (PMN) ferroelectric ceramics exhibit high performance in many aspects. These kinds of ferroelectric ceramics are currently used as driver material, and also a potential sensing material for the excellent electrostrictive property and lower loss [4–6]. As we all know, differences are existing in the behavior of electrical ceramics with various thickness [7]. The electrical ceramics in the form of bulk-like, thin film and single crystal have been widely investigated. However, thin film electrical ceramics don't process high performance in dielectric performance as well as bulk like due to the dead layer in the interface.

Air plasma spraying (APS) provides an effective way to obtain 'bulk-like' thickness hard coatings. The thick coatings result in elevated lifetime as compared with the bare substrate components. Wear, corrosion and thermal resistance coatings are always fabricated by this technology during the recent years. With the development of this technology, a broad range of electrical materials (thermoelectric [8], dielectric [9,10], semi-conducting [11], insulating [12] et al.), have been used to fabricate coating via plasma spray to cater for different functional requirements. However, the unique influences such as extremely high temperature, rapid cooling, and reducing atmosphere (H_2) et al. lead to unexpected either advantage or disadvantage variation in properties. Wasoo [8] in-situ synthesized sub-stoichiometry TiO_{2-x} coatings properties by plasma spray. Oxygen deficiencies and corresponding crystal lattice defects caused by the reducing H_2 lead to thermoelectric properties. Plasma sprayed $BaZrO_3$ coatings with excellent infrared radiative properties but was accompanied with $BaCO_3$ [13], due to the decomposition in the extremely high temperature. As is known, both of micro-defect and crystal lattice distortion can affect the performance of electrical ceramic. Many attempts have been made to fabricate the PZT-based ceramic coatings [14–17]. Hassler [15] suggested sever volatility of PbO because of the extremely high-energy environment and the low thermostability of these materials. The volatility of PbO not only leads to the inhomogeneous distribution of the phases, but also leads to the formation of pores. The same results have been reported by Pavel [16] as well. It has been known that defects such as pores and cracks have great influence on mechanical and physical properties. Besides that, porosity and microstructure caused by the volatilization of PbO during plasma spraying lead to sever behavior on elastic modulus and hardness [18].

It is important to obtain compact structure and homogenous phase, hence, dielectric performance of PZT-based coatings is

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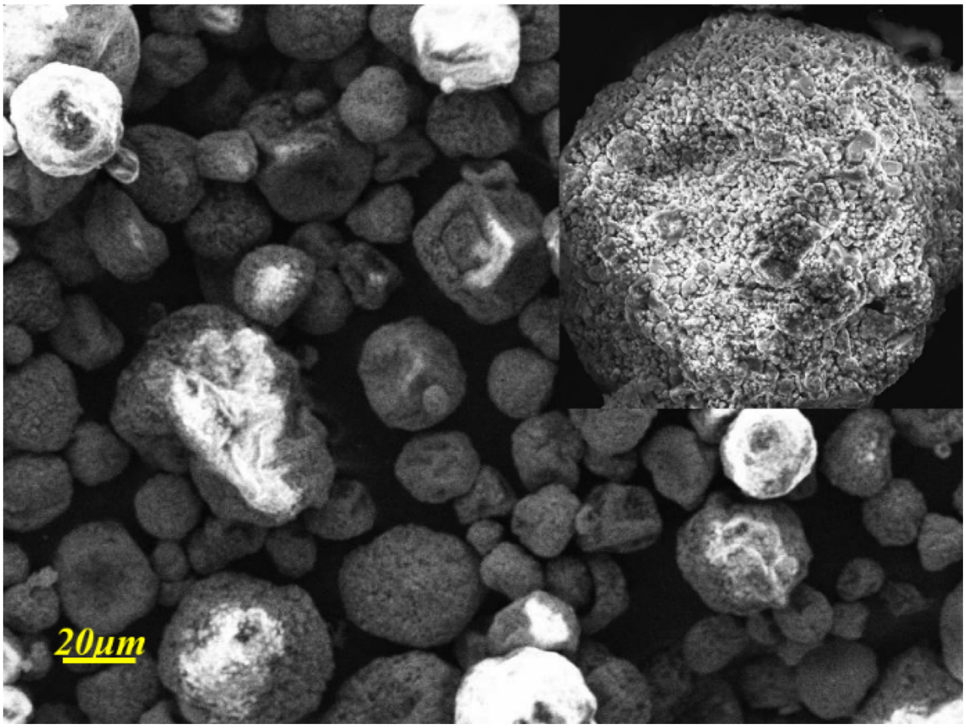

Fig. 1. Morphology of PZT-PMN powders.

expected to be enhanced [19,20]. Post heat treatment is one of effective methods which is always used to reduce the pores and micro-cracks in plasma sprayed coatings. In the later research of Pavel [16], the PZT ceramic coatings after treated at 850 °C exhibited a better performance on crystallinity, but were accompanied with relatively high porosity (porosity ≈ 14.8%) and numbers of inhomogeneity, which can been distinguished by colors within the structure. In general, plasma spraying process and simple thermal post treatment is not essential to obtain PZT-based coatings with compact structure. A method to obtain coatings with less porosity is required. Supersonic plasma spraying system (PlzaJet) was first developed in 1986 by Browning, USA. It is reported as an effective way to fabricate ceramic coatings with less porosity compared to well-established thermal spray methods [21,22]. Due to the unique design of spray-gun structure, the particles can reach or even higher than velocity of sound in the effective distance. Therefore, leading to dense microstructure and continuously graded change of mechanical and physical properties. Han [23] reported the CeO_2-Y_2O_3-ZrO_2 graded thermal barrier coatings fabricated by supersonic plasma spraying technology process dense structure, high bonding strength and homogeneity in component. It is expected that PZT-PMN particles will be heated sufficiently in short time and well splashed on the substrates by supersonic plasma spraying technology, hence, volatilization and porosity in as-sprayed coatings will be reduced.

The goal of the attempts was to obtain a compact as-sprayed PZT-PMN coatings and high dielectric performance via supersonic plasma spraying technology. Post heat treatment was used to further reduce the pores and eliminate the inhomogeneity in component. The focus of the present paper is to carry out a detail study of the phase transition and micro-defect evolution.

2. Experiment

2.1. Fabrication of powder and ceramic coatings

In order to make the powder applicable for plasma spray, the bulk PZT-PMN ceramics were crushed into tiny particles with the average size of 300 nm and finally bonded by PVA (Fig. 1). The feed powders, varied from 50 μm to 80 μm, are shown in Fig. 1-b, which may exhibit good feeding performance in the process of plasma spray. Each of the powders is composed of several nan-sized particles.

Raw material powders, Pb_3O_4, $MgCO_3$, Nb_2O_5, TiO_2 and ZrO_2, were weighed by the ratio $0.5(Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.5Pb(Zr_{0.48}Ti_{0.52})O_3)$ and mixed together by ball-milling, then dried. The mixture was sintered at 550 °C for 2 h, 850 °C for 2 h and ball-milled for 24 h respectively. PVA was mixed with ball-milled powders and then pressed into disks. The green pellets were burned out at 800 °C for 1 h and then sintered at 1300 °C for 2 h. The calcined ceramic powders were crushed into nan-size, and then mixed with binder (PVA), water and Pb_3O_4. According to the previous research 10 wt% extra Pb_3O_4 was effective to reduce the volatilization of PbO of PZT-based coatings. The mixture was dried in a centrifugal spray dryer at speed of 13,000 rpm to achieve the desired distribution of particle size. Carbon steel, previously cleaned with acetone or alcohol solution, and sand-blasted with alumina particles, was used as the substrate with dimensions of 60 mm × 30 mm × 5 mm. The ceramic powders were sprayed on substrates by supersonic plasma spray system. The equipment is developed by the National Key Laboratory for Remanufacturing, China. The spray process was conducted at ambient pressure using Ar ($3.4\,m^3\,h^{-1}$) and H_2 $0.5(m^3\,h^{-1})$ with plasma power of 48 kW (400A and 120V), powder feeding rate of 30 g/min and spraying distance of 75 mm. The as-sprayed coatings were subsequently treated at 450 °C, 550 °C and 650 °C for 6 h in atmospheric environment. The coatings were abbreviated as C450, C550 and C650 respectively.

2.2. Measurement and characterization

The crystal structure of the ceramic powder and coatings (untreated, treated at 450 °C and 550 °C) was examined by X-ray diffraction XRD with Cu Kα (1.54056 Å) radiation on a Philips analytical diffract meter. The morphology of the coatings was

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