Influence of synthesis temperatures on the crystalline grain growth and morphology of lanthanum magnesium hexaaluminate☆

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ABSTRACT

Lanthanum magnesium hexaaluminate (LaMgAl$_{11}$O$_{19}$, LMA) was prepared at different temperatures by solid-state reaction. Phase compositions and crystal morphologies of specimens synthesized at different temperatures were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM). It was observed that the crystalline grain size of LMA was not only dependent on the preparation temperature but also on its powder morphology. In the temperature range of 1300−1550 °C, LMA showed platelet grain and the average crystalline grain size increases with the increase in temperature. At 1600 °C, if the powder was sintered for two times, the equiaxed grain could be found with the decrease in grain space, resulting in the reduction of the crystalline grain size. Styles of specimens (powder or disk) might have no obvious influence on morphologies and sizes of LMA crystalline grains which were synthesized with the well-dispersed raw material mixtures. The synthesis temperature played a key role in influencing the free space for the formation and growth of crystalline grains.

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1. Introduction

Thermal barrier coatings (TBCs) are frequently sprayed on the surface of superalloy substrate to improve the operating temperature and fuel efficiency of gas turbines.[1,2] As a traditional TBCs material, yttria partially stabilized zirconia (YSZ) is the commonly used ceramic top-coat material due to its low thermal conductivity and relatively high thermal expansion coefficient (CTE). Nowadays, with the development of industry, it is desperately necessary to develop TBCs with the higher operating temperature and the longer lifetime. YSZ coatings may encounter phase transformation, serious sintering in combination with the increase of Young's modulus at temperatures higher than 1200 °C, which limits their applications.[3] It is a tendency to improve the temperature capability and durability of TBCs by developing new materials and structures. New TBCs materials, such as, rare earth zirconates with

pyrochlore-type structure which has high phase stability and sintering resistance have been developed to improve the operating temperature.[4−6] Besides, new TBCs structures have been designed to prolong the thermal cycling lifetime, such as LaMgAl$_{11}$O$_{19}$/YSZ double ceramic top-coat systems which exhibit improved strain tolerance and thermal cycling lifetime in comparison with single layer YSZ or LMA coatings.[7]

LMA with a magnetoplumbite structure has high melting point, large thermal expansion coefficient, significantly low oxygen ion diffusion, and low thermal conductivity. It has been extensively studied as an important candidate material to be applied in industries, the military and scientific research, active elements of solid-state lasers.[8−13] As a TBCs material, it possesses long-term structural and thermochemical stabilities up to 1400 °C. In particular, LMA has significantly lower sintering rates than zirconia-based materials for its typical structure characteristics that the highly charged La^{3+} cation locates in an oxygen position in the hexagonal close-packed structure of oxygen ions. The ion diffusion is strongly suppressed vertically to the crystallographic *c*-axis, which is related to its platelet crystal.[12,14−18] Currently, solid-state reaction is the most widely used method to prepare LMA powders.[7,8,14,15] High temperature is the decisive factor to synthesize

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the single-phase LMA. In fact, at 1600 °C, there is still a small amount of the second phase $LaAlO_3$ with a perovskite structure by solid-state reaction of La_2O_3, MgO, and Al_2O_3. As a result, increasing the synthesis temperature and pressure[19] becomes the main method to reduce the formation of $LaAlO_3$. Besides, it is not clear about the influence of $LaAlO_3$ on the properties of LMA coatings. As we all know, partly amorphous phase easily forms in the as-sprayed coating for the rapid quenching from the molten state during plasma spraying and the amorphous phase will recrystallize after heating.[3,13] The recrystallization of the amorphous phase in LMA coatings will cause a serious volume contraction[16] and then decrease their service lifetimes. The crystalline grain size affects the melting state of powders, leading to the change of the amorphous phase content. The crystalline grain size is affected by morphologies of the crystals which have a relationship to contact areas between raw materials in green specimens as well as with the free space available for LMA crystalline grains to grow. In addition, for hexaaluminates the thinner the platelet crystals are, the better thermal-shock resistance coatings have because more interstices are retained in the sintered specimen.[14] Considering the effects of the crystalline grain size, the platelet crystal thickness and the purity of the feedstock on LMA coatings, investigating the relationship of the three factors and the synthesis temperature of LMA powders can provide some useful information on the formation and the content of the amorphous phase during plasma spraying, which is good for prolonging its service life. However, there are few systematic investigations into the variation on the crystalline grain size with the synthesis temperature of LMA.

In this paper, raw material mixtures after being ball-milled with two conditions (powder and disk) are used to synthesize LMA by two steps at different temperatures. The variations in phase compositions, crystalline grain sizes, and morphologies in the powders and disks with the temperatures are investigated at different stages. The growth mechanisms of crystalline grains of different steps are analyzed.

2. Experimental

As the main chemicals in this work, La_2O_3, MgO and Al_2O_3 were heated at 1000 °C for 2 h to remove H_2O and CO_2 adsorbed in the raw materials. The stoichiometric amounts of raw materials were mixed with deionized water for 24 h by ball-milling and were dried later. The dried powders were synthesized for one time at 1600, 1550, 1500, 1450, 1400, 1350 and 1300 °C for 12 h, respectively, to synthesize seven groups of LMA powders. The powders which were synthesized for one time were named as LMA-P-1-1600, LMA-P-1-1550, LMA-P-1-1500, LMA-P-1-1450, LMA-P-1-1400, LMA-P-1-1350, and LMA-P-1-1300. Then, these LMA powders were ball-milled and synthesized for the second time and the as-synthesized powders were named as LMA-P-2-1600, LMA-P-2-1550, LMA-P-2-1500, LMA-P-2-1450, LMA-P-2-1400, LMA-P-2-1350, and LMA-P-2-1300. Besides, raw material mixtures were pressed under a pressure of 20 MPa to form disks with a diameter of 12 mm. Then, these disks were sintered at 1600, 1550, 1500, 1450, 1400, 1350 and 1300 °C for 12 h, respectively, and this process also proceeded at two times without intermediate ball-milling. Similarly, disks sintered for one time were named as LMA-D-1-1600, LMA-D-1-1550, LMA-D-1-1500, LMA-D-1-1450, LMA-D-1-1400, LMA-D-1-1350, and LMA-D-1-1300. Naturally, disks sintered for two times were named as LMA-D-2-1600, LMA-D-2-1550, LMA-D-2-1500, LMA-D-2-1450, LMA-D-2-1400, LMA-D-2-1350, and LMA-D-2-1300, respectively.

Thermogravimetric (TG) and differential scanning calorimetry (DSC) of the raw material mixtures after ball-milling and drying were performed on a thermoanalyzer (STA 449F3) in air

atmosphere with a heating rate of 10 °C/min. Microstructures of the synthesized powders and disks were characterized by a scanning electron microscope (SEM, QUANTA FEG 450). Meanwhile, the average thickness and aspect ratio of the platelet crystals in LMA-P-2 and LMA-D-2 were analyzed using SEM micrographs. Phase compositions of LMA powders and disks synthesized at different stages were identified by X-ray diffraction (XRD, D/MAX-RB RU-200B, Cu-Kα radiation, $\lambda = 0.15406$ nm) over 2θ values of 15–65° with a scanning rate of 4°/min and a step width of 0.02°. A small quantity of graphite powder was mixed with the synthesized powders for the calibration of XRD. The crystalline grain size was calculated using Scherrer's Equation, and the effects of the machine broadening were eliminated. Densities of specimens in LMA-D-1 and LMA-D-2 were determined by a bulk weight/volume method. Porosities of the specimens in LMA-D-1 were evaluated by image analyses. The molar fraction of $LaAlO_3$ was calculated by the following equation:

$$M_{LaAlO_3}\% = \frac{I_{LaAlO_3}}{I_{LaAlO_3} + 0.5(I_{107} + I_{114})} \times 100\% \tag{1}$$

where M is the molar fraction of the phase and I is the intensity of a given peak.

3. Results and discussion

3.1. Crystalline grain growth in LMA powders

The formation mechanism of LMA with the raw materials of La_2O_3, MgO and Al_2O_3 by solid-state reaction can be summarized as follows: at first, La_2O_3 reacts with Al_2O_3 to form $LaAlO_3$ at approximately 900 °C, and then $LaAlO_3$ reacts with Al_2O_3 and $MgAl_2O_4$ to produce LMA at approximately 1200 °C.[20] As shown in the DSC curve (see in Fig. 1), there is an exothermic peak at 1185 °C, which is close to the formation temperature of LMA with the raw materials of La_2O_3, MgO, and Al_2O_3 by solid–state reaction. There is an endothermic peak at 361 °C in the DSC curve, corresponding to a mass loss of about 7.81% in the TG curve. The endothermic peak may correspond to the step-by-step decomposition of hydroxides, which is formed by the raw materials during the ball-milling. Fig. 2 shows the XRD patterns of LMA-P-1 sets and LMA-P-2 sets. Except that $LaAlO_3$ is the main phase, the XRD pattern of LMA-P-1-1300 coincides with the JCPDS card 26-0873, indicating that the LMA phase starts to form at 1300 °C. With the increase in the synthesis temperature, the peak intensity of $LaAlO_3$ phase decreases. Besides,
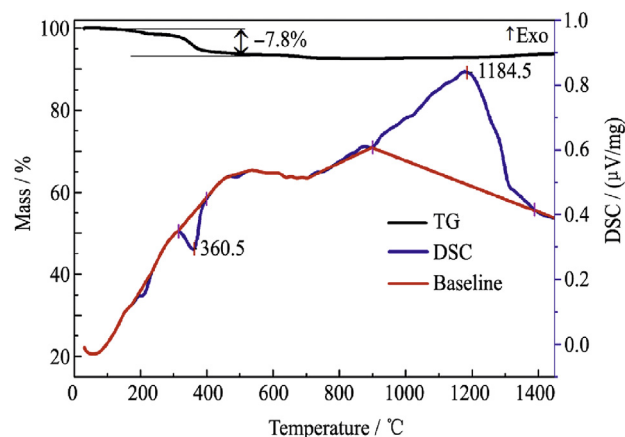

Fig. 1. DSC and TG curves for the mixture of raw materials after ball-milling and drying.