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Industrial growth of yttria-stabilized cubic zirconia crystals by skull melting process

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Abstract: We reported the development of a Φ100 cm growth apparatus for skull melting growth of yttria-stabilized cubic zirconia (YSZ) crystals and more than 1000 kg crystals have been grown in the furnace each time. The growth conditions were optimized and the structure of the as-grown crystals was characterized by X-ray diffraction. The transmittance of 15 mol.% yttria-stabilized cubic zirconia crystal was nearly 80% in the range of 400–1600 nm. The refractive indices were measured and fitted the Sellmeier equation which was obtained by least-squares method. The results showed that the apparatus was very suitable for industrial growth of YSZ crystals.

Keywords: yttria-stabilized cubic zirconia; crystal growth; skull melting process; rare earths

Single crystal ZrO_2 is an important gem material due to its high index of refraction and polycrystalline ZrO_2 ceramics is commonly known as structural and functional materials having high strength, hardness, heat resistance, and resistance to corrosive media. However, there are three polymorphous modifications of ZrO_2: monoclinic, tetragonal, and cubic. The latter two are high-temperature modifications, but they can be stabilized at lower temperatures by introducing di- and trivalent metal oxides like CaO, MgO, Y_2O_3, and others. Among them, yttria stabilized cubic zirconia (YSZ) has received much attention due to its high fracture toughness, excellent oxygen conductivity, low thermal conductivity and stability at high temperatures for many important applications, such as the electrolyte for solid oxide fuel cells (SOFC), superconductor substrates and artificial gem (imitation diamond)[1–5].

The high melting point and high quality requirements constitute enormous conditions unsuited for the melting and crystallization of cubic zirconia in conventional metallic or graphite crucibles. In 1969, French researchers firstly reported the growth of relatively large (1.27 cm long) cubic zirconia crystals using a new technique called “skull melting”[6]. In the early 1970s, scientists at the Lebedev Physical Institute (Moscow) expanded this new technique, and identified the unique properties of cubic zirconia[7]. In 1977, a new diamond stimulant called “Russian diamond” was launched into the market and warmly welcomed by the consumers[1]. Since then on, YSZ crystal becomes a more and more important artificial gem material and many kinds of product have been developed. In China, study on the growth of YSZ crystals was carried out by Zhang et al. from Shanghai Institute of Ceramics, Chinese Academy of Sciences in the early 1980s[8]. YSZ gems in China have undergone dramatic development in the transition from laboratory-scale crystal growth to industrial-scale production[9]. At present, the annual output of YSZ crystals is estimated to be 4500 t in the world and half of the production is fabricated in China[5]. The great market promotes improvement of the traditional growth technology so that YSZ can be grown with low cost and high yield. In this paper, the development of a novel industrial growth apparatus and the growth results of YSZ crystal were reported.

1 Experimental

1.1 Materials

A large growth apparatus was developed for industrial growth of YSZ crystal. A palisade-like wall consisting of water-cooled copper tubes formed the growth container with an inner diameter of about 100 cm and a height of 80 cm. A radio frequency (RF) coil is assembled around the palisade-like wall to heat up the charge. High-purity ZrO_2 powder and about 15–20 mol.% Y_2O_3 were mixed thoroughly

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and put into the container. Several graphite sticks were connected into a circle for initial heating. The raw materials became electric conductor when the temperature reached above 1200°C. Then a melt pool was formed, and the raw materials were heated by eddy current. The melt pool became bigger and bigger and finally all the powders were melted completely except for the skull.

The radio frequency (RF) generator works in a frequency range of 800 kHz–1 MHz with a power of about 600 kW. When a stable temperature formed in the melt, the lowering mechanism started to work at a lowering rate of 5–15 mm/h. So the crucible was slowly lowered out of the heating field, and the melt crystallized from the bottom to the top. After the crystal growth finished, the container was cooled down to room temperature. The as-grown ingot was taken out from the container and ZrO_2 crystals were separated by lightly beating with a hammer. During the growth process, the raw materials were continuously added to the container by a hopper feeding system. Using this technique, the total charge can reach 1000 kg and large crystals can be grown. The growth cycle is about 50 h.

1.2 Characterization

The as-grown YSZ crystal was cut into several pieces and ground into fine powders. Powder X-ray diffraction was carried out by means of Rigaku D/Max-2550V diffract-meter (Japan) from 10° to 80° (2θ) with Cu Kα radiation at room temperature. YSZ crystal sample of 4 mm thickness was prepared and the two main surfaces were polished. The transmittance spectrum was measured using Varian's Cary 500 UV-VIS-NIR spectrophotometer at room temperature from 300 nm to 1650 nm. The refractive indices n and the extinction coefficients k were measured using Jobin Yvon UVISEL/460-VIS-AGAS ellipsometer (France) in the range of 300–1650 nm.

2 Results and discussion

2.1 Crystal growth

Inductive skull melting of zirconia is based on direct induction heating of the electrically conducting melt by alternating electromagnetic field. However, ZrO_2 has poor conductivity under 1200 ºC and some strips of Zr metal were used in the traditional growth process. In our experiment, cheap graphite instead of Zr strips was used. As a direct induction heating method, the required electrical power strongly depends on the chosen working frequency, which must be adjusted according to the electrical conductivity of the melt and the size of the crucible. For large-size crucible, it is difficult to get a stable and homogeneous melt at high frequency of about 2 MHz, which was used previously[10]. By using the graphite to form a melt pool, the RF generator can work in a frequency range of 800 kHz–1 MHz. Thus, a stable melt can be easily obtained after holding for 2–3 h. Due to the large diameter of the crucible, the raw materials were fed for several times during the growth process. After all the raw materials were melted and gradually crystallized, the power input was reduced. The ingot was cooled down and the as-grown crystals were taken off. Fig. 1 shows the as-grown ingot and Fig. 2 shows a typical YSZ crystal with a length of 178 mm. The crystal looks transparent without inclusions or air bubbles. On the top of the sample, there is an opaque layer with a thickness of 15 mm, which was crystallized from the residual melt.

2.2 Crystal structure

In order to determine the crystal structure, the initial part A and the end part B of the typical sample were cut and ground into fine powders for X-ray powder diffraction (XRD). Fig. 3 shows the XRD patterns of parts A and B. The XRD patterns of the two different parts are the same and all the peaks completely accord with those of $Y_{0.15}Zr_{0.85}O_{1.93}$ phase reported in the standard XRD card (JCPDS 30-1468). It demonstrates that the crystal has cubic structure with cell pa-

Fig. 1 As-grown YSZ ingot with a diameter of 100 cm and a height of 80 cm

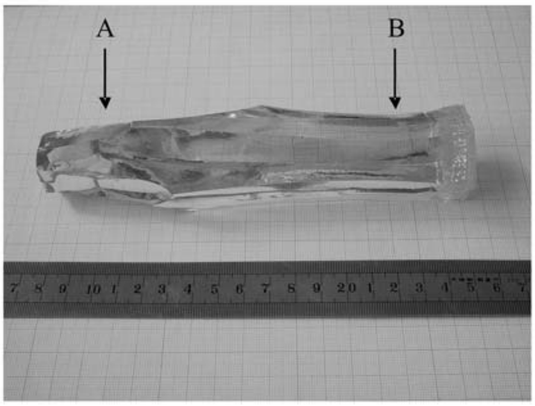

Fig. 2 A typical YSZ crystal of Φ25 mm×180 mm