JOURNAL OF MATERIALS SCIENCE 28 (1993) 1659–1662

The growth of single-crystal fibres directly from source rods made of ultrafine powders

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By means of the laser-heated pedestal growth (LHPG) method, the growth of single-crystal fibres directly from source rods made of ultrafine powders is studied in this paper. The ultrafine powders were obtained by the sol–gel method and then were pressed into plates at room temperature. The source rods were simply cut from the plates. The advantages of this new technique are (i) good homogeneous source rods can be obtained because all components are mixed with their acid solutions, and the composition in the crystalline fibre grown from a source rod by the LHPG method will be uniform due to its high growth rate (1–2 mm min^{-1}); (ii) the densified source rods can be pressed at room temperature since ultrafine powders are used, so contamination due to hot pressing or melting can be avoided; and (iii) highly doped crystal fibres can be easily obtained.

1. Introduction

Single-crystal fibres are usually grown from their bulk crystals. They combine not only the good physical and optical properties of single crystals, but also the characteristics of fibres in optical conduction and shape for connectivity. Therefore they can be made into a series of optical fibre devices with various functions such as fibre sensors and fibre lasers, which can be widely applied in fibre communication, temperature measurement, laser transmission and non-linear optics as well as in metallurgy, the chemical industry and medical treatment. More and more people are interested in this research. However, there are still many problems in improving the qualities of crystalline fibres and developing other new kinds of crystal fibre. As said above, single-crystal fibres are grown out of their bulk crystals, which will not only make the grown crystal fibres easily inherit the original defects of the bulk crystals, but also limit the development of new crystal fibres. Tang *et al.* [1] have grown single-crystal fibres from a hot-pressed source rod, which made a great advance in this research. However, there are still some problems which have not been solved. First, the materials are mixed in their powder form, so the composition cannot be uniform, and second, contamination from hot contact is unavoidable.

In this paper three kinds of ultrafine powder, Al_2O_3, $Cr–Al_2O_3$ and $Ti–Al_2O_3$, were first made by the sol–gel method and then pressed into plates by cold pressing. The source rods were simply cut from these plates. With these source rods, three types of single-crystal fibre (Al_2O_3, $Cr–Al_2O_3$ and $Ti–Al_2O_3$) were successfully grown with the help of the laser-heated pedestal growth (LHPG) technique.

2. Experimental procedure and results

2.1. Preparation and synthesis of ultrapowders

Sol was prepared in an $Al(NO_3)–H_2O–(CH_2)_6N_4$ system. Aluminium nitrate, $Al(NO_3)_3 \cdot 9H_2O$, dissolved in water was used as raw material, and hexamethylenetetramine, $(CH_2)_6N_4$, was used as the catalytic agent. The sol was then warmed in a 50 °C water bath until gelation [2]:

$$(CH_2)_6N_4 + H_2O \xrightarrow{\text{Heating}} 6HCHO + 4NH_3$$

After this reaction a transparent gel was formed, and thereafter dried in an oven at 110 °C for 24 h. An amorphous Al_2O_3 ultrafine powder was obtained. With X-ray diffraction analysis, it was identified as non-crystalline Al_2O_3. If a step heat treatment is used, then α-Al_2O_3 can be obtained after the powder is heated above 980 °C (Fig. 1). The powder phase transformation process during the step heat treatment was determined by a model D/Max-RA X-ray diffractometer made in Japan. Its transformation is as follows:

$$\text{Amorphous } Al_2O_3 \xrightarrow{\text{Heating}} \gamma\text{-}Al_2O_3 \xrightarrow{\leqslant 750\,^\circ C} \theta\text{-}Al_2O_3 \xrightarrow{\leqslant 980\,^\circ C} \alpha\text{-}Al_2O_3$$

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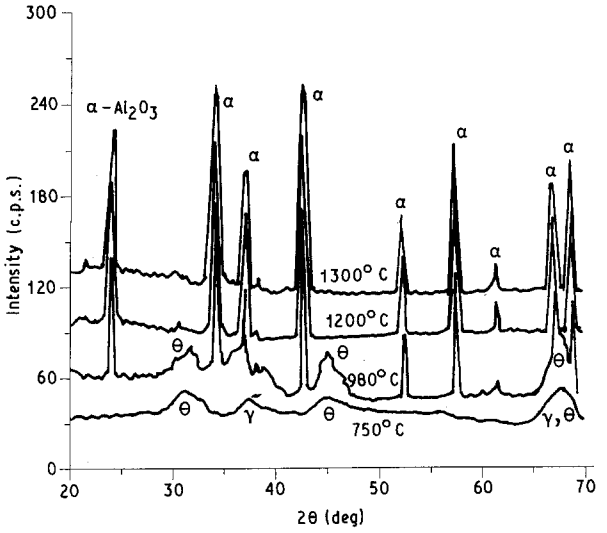

Figure 1 X-ray diffraction patterns of Al_2O_3 ultrafine powder during the heat-treatment process.

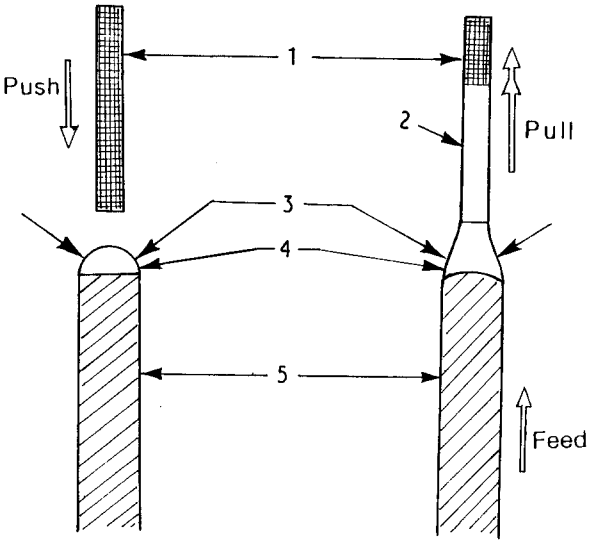

Figure 2 Schematic diagram of laser-heated pedestal growth: (1) seed crystal, (2) grown crystal fibre, (3) CO_2 laser beam, (4) melting zone, (5) source rod.

With the help of a model LKY-2 microparticle analyser, the average particle size of the powder is measured as 0.69 μm.

By the sol–gel method as stated above, three types of ultrafine powder, pure Al_2O_3, Al_2O_3 + 1 wt % Cr_2O_3 and Al_2O_3 + 0.5 wt % Ti_2O_3, were synthesized. These powders were finally pressed into plates by cold pressing, and source rods with a cross-section 2 mm × 2 mm were cut from the plates.

2.2. Growth of single-crystal fibres

The LHPG method was used for crystal fibre growth, using pure Al_2O_3 single-crystal fibre as its seed. At the beginning, the power of the CO_2 laser beam was slowly increased till a half-ball melting zone was formed. The seed was pushed into the zone. Then the power of the laser beam was readjusted until a suitable melting-zone shape was obtained. Finally, the growing velocity of the crystal fibre and the feeding velocity of the source rod were slowly increased at the same time and readjusted until a suitable ratio between the growing velocity and the feeding velocity was achieved (Fig. 2). In this experiment, this velocity ratio is about 2.5–5.0, which is a little smaller than for growth directly from a single crystal (in general 4.0–9.0, which is related to the surface tension of the melt; different ratios should be used for different materials, e.g. it is 7.0–9.0 for Al_2O_3) [3, 4]. A uniform crystalline fibre with diameter 0.90 mm was directly grown from the source rod of ultrafine powder (with cross-section of 2 mm × 2 mm) when the velocity ratio was 4.4. The greater the ratio, the smaller is the diameter of the grown crystal fibre.

With the help of X-ray Laue photography, the grown crystal fibres were identified as single crystals. Fig. 3 shows the Laue spots of the grown Al_2O_3 crystal fibre.

Defect inspection was carried out with metalloscopy. The results showed that single-crystal fibres with few defects can be obtained through a suitable choice of the growing parameters (Fig. 4)

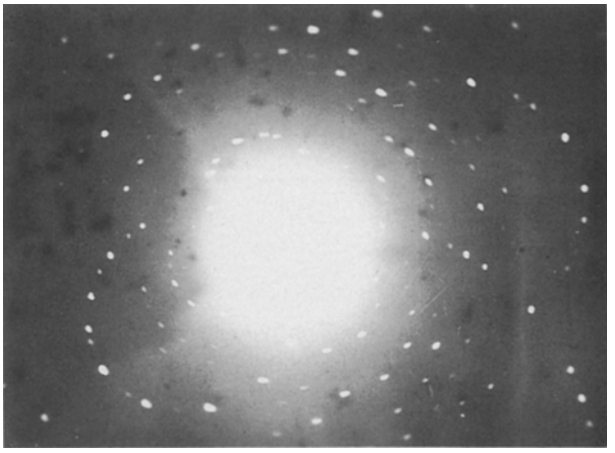

Figure 3 X-ray Laue spots for the grown Al_2O_3 crystal fibre.

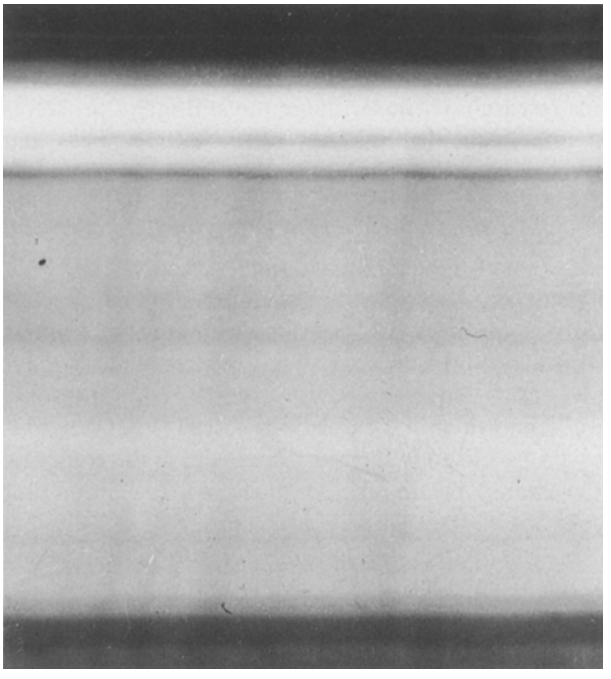

Figure 4 Metallograph of the grown Al_2O_3 crystal fibre (260 ×).

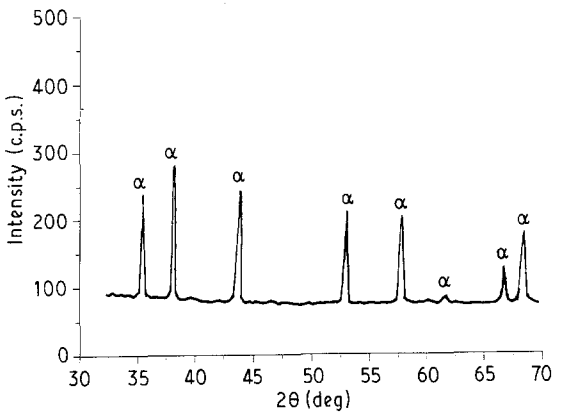

Figure 5 X-ray diffraction pattern of the grown Al_2O_3 crystal fibre.

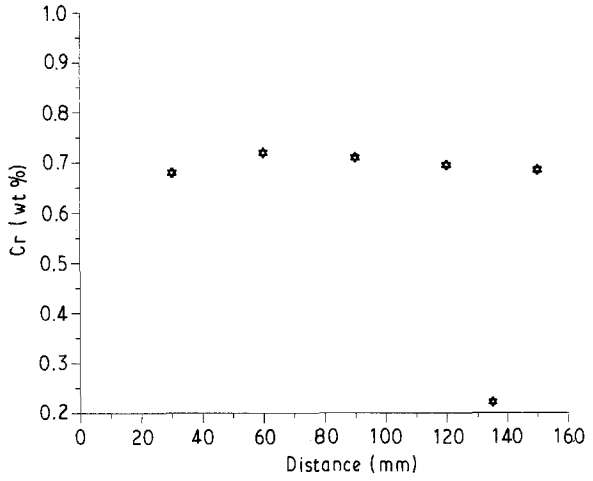

Figure 6 Concentration distribution of doped Cr impurity along the longitudinal direction of grown Cr–Al_2O_3 crystal fibre.

X-ray diffraction results for the grown Al_2O_3 crystal fibre show that the crystal fibre is entirely composed of α-Al_2O_3 (Fig. 5). This is because the ultrafine powder will be wholly transformed into pure α-Al_2O_3 only if it is heated above 980 °C, while the powder will be heated above its melting point (2050 °C) when the single-crystal fibre is grown from it.

The chemical compositions of Cr and Ti in the grown Cr–Al_2O_3 and Ti–Al_2O_3 crystal fibres were analysed by electron probe micro-analysis (EPMA) and found to be uniform along the length of the crystal fibres. The results for Cr distribution in the grown Cr–Al_2O_3 crystal fibre is shown in Fig. 6. It can be seen that the compositional fluctuation of Cr is smaller than 5%, which is less than the requirements for laser devices [5].

3. Discussion

The experimental results have shown that single-crystal fibres can be grown directly from source rods made of ultrafine powders which were synthesised with help of sol agglutination.

3.1. Choice of growth parameters

From the results of microparticle analysis, the average particle size of the ultrafine powders is only 0.69 μm; they are non-crystalline from X-ray analysis. Therefore they are easily shaped through cold pressing and formed into source rods with a higher density (the relative density is 76%). Because this density is near to that of crystalline fibres and is uniform, single-crystal fibres can be easily grown with only a suitable adjustment of the ratio between the growing velocity and the feeding velocity. The growing velocity can still be kept high (here 1.6 mm min^{-1}). These rules for growing are similar to those of the crystal fibre growth process in which crystals were used as source rods [3, 4]. The difference is that the ratio between the growing velocity and the feeding velocity should be a little smaller if all other conditions are the same. This is because the relative density of the source rod is always smaller than unity (i.e. the density of the grown crystal fibre is always greater than that of the source rod made of ultrafine powder, although they can be nearly equal).

From mass equilibrium

$$A_f V_f \rho_f = A_s V_s \rho_s \quad (1)$$

where A_f is the cross-sectional area of the grown crystal fibre and A_s is that of the source rod, V_f is the growing (pulling) velocity of the crystal fibre, V_s is the feeding velocity of the source rod, ρ_f is the density of the grown crystal fibre and ρ_s is that of the source rod. If the cross-sections of the grown crystal fibre and the source rod are both round and their diameters are d and D, respectively, and if the crystal fibre is grown directly from the same bulk crystal, $\rho_f = \rho_s$. Then from Equation 1

$$\pi\left(\frac{d}{2}\right)^2 V_f = \pi\left(\frac{D}{2}\right)^2 V_s$$

i.e.

$$\frac{V_f}{V_s} = \left(\frac{D}{d}\right)^2 \quad (2)$$

This is the equation for the crystal fibre growth process in which the bulk crystal is used as the source rod [3, 4].

In our experiments, the source rod was pressed from ultrafine powder. We obtained

$$\rho_s = 0.76\ \rho_f$$
$$A_f = \pi(d/2)^2$$
$$A_s = 2\ \text{mm} \times 2\ \text{mm}$$

if

$$V_f/V_s = 4.4$$

From Equation 1, the diameter of the grown crystal fibre can be calculated as follows:

$$d = 2\left[A_s\left(\frac{\rho_s}{\rho_f}\right)\left(\frac{V_f}{V_s}\right)^{-1}\pi^{-1}\right]^{1/2}$$
$$= 0.94\ \text{mm}.$$

The diameter of the grown crystal fibre is a little smaller than its calculated value, which can be attributed to the slight evaporation of atoms from the part of the surface which is irradiated by the laser beam.

In summary, single-crystal fibres can be easily grown directly from source rods made of ultrafine powders if the growing parameters are suitably chosen. Contamination is avoided since neither sintering nor a melting process was used before the single-crystal fibre growing process by means of the laser-heated pedestal growth method.

3.2. Solute distribution

The growing velocity for single-crystal fibres is usually very great (more than 1–2 mm min^{-1}). The solute segregation in solidification is a non-equilibrium process [6]. Therefore the solute distribution in the grown crystal fibre is very similar to that in its source rod [7], so a uniform distribution of solute in the source rod used is most important to obtain a homogeneous crystal fibre. In general, single-crystal fibres are grown directly from bulk crystals which are grown at a very small velocity (0.05 mm min^{-1}) and the distribution of solute in the grown crystal cannot be uniform [6]. Therefore if bulk crystals are used as source rods, the grown crystal fibres will unavoidably inherit the non-homogeneous defects of the solute in the bulk crystals used. Tang *et al.* [1] have grown single-crystal fibres directly from a source rod made of powders by hot pressing. This is an advantageous attempt in the improvement of the properties of single-crystal fibres, but the composition of the source rod cannot be very homogeneous since the powders were only mechanically mixed in their solid state. However, the source rods used here were made of ultrafine powders by cold pressing, while the ultrafine powders were synthesized by sol agglutination in which all components could be fully mixed since they were in solution. So the distribution of solute in the source rods is very much more homogeneous. The distribution of solute in the crystal fibres grown directly from the source rods was also uniform (see Fig. 6).

3.3. Doped fibres

For $Cr-Al_2O_3$ bulk crystal grown by the Czochralski method, the content of Cr in the crystal is very small [5]. Otherwise its distribution in the crystal cannot be kept uniform. In our experiments, not only is there high purity in the source rods used because they were cold-pressed from ultrafine powders synthesized by means of sol agglutination, but also there is a large temperature gradient in the melting zone and the crystal growing velocity can be very high (1–2 mm min^{-1}). Therefore although the doped concentration of Cr in the source rods is much higher than in the usual ruby crystal, the distribution of Cr in the grown crystal fibres is still uniform (see Fig. 6). So single-crystal fibres with highly doped and uniformly distributed solute can be obtained by this method. Nevertheless, source rods with a highly doped and uniformly distributed solute are first necessary. The method proposed and studied in this paper seems to be the best one yet for us to obtain single-crystal fibres with a highly doped solute.

4. Conclusions

With the help of the LHPG technique, single-crystal fibres with highly doped and uniformly distributed solute can be successfully grown directly from source rods cold-pressed from ultrafine powders synthesized by the method of sol agglutination. The advantages of this new technique are (i) the distribution of solute in the grown crystal fibres is much more uniform because a large growing velocity and homogeneous source rods are used; (ii) contamination is efficiently avoided because the source rods can be easily pressed from non-crystalline ultrafine powders and neither hot pressing nor melting is used; and (iii) highly doped crystal fibres can be easily obtained.

Acknowledgements

The able technical assistance of Hui Yang of the Materials Department, Zhejiang University for the preparation of the source rods used in the experiments is greatly appreciated. The authors are pleased to acknowledge the support of Zhejiang Provincial Scientific and Technological Community (grant 1989).

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Received 12 February
and accepted 11 August 1992