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Oxide Crystal Growth using Gas Lasers

D. B. GASSON, B. COCKAYNE
Royal Radar Establishment, Malvern, Worcs, UK

The use of CO_2-N_2-He gas lasers as a heat source in a floating-zone recrystallisation technique of crystal growth is described. So far, single crystals of Y_2O_3, $CaZrO_3$, $MgAl_2O_4$ and Al_2O_3 have been grown in this manner and factors controlling their quality are discussed. The problems associated with this technique of crystal growth are reviewed.

1. Introduction

In recent years, several crucible-free techniques for growing oxide crystals from the melt have been developed. These techniques have generally been based upon either the floating-zone or pedestal principles and several types of heat source have been used to form the respective molten zone or pedestal cap. These include electron beams generated from both hot and cold cathodes [1-3], thermally imaged arcs [4], arc plasmas [5] and gas burners [6]. Several of these methods are claimed to be useful for oxides with melting points in the temperature range 1500 to 3000° C but, in practice, crystal growth has usually been demonstrated with Al_2O_3 (MP = 2050° C) or materials which melt at lower temperatures. The present paper examines the use of CO_2-N_2-He gas lasers as a heat source in the floating-zone recrystallisation technique of crystal growth for oxides which melt within the temperature range 2000 to 2450° C.

CO_2-N_2-He gas lasers offer several important advantages over other heating systems used in oxide crystal growth. For instance, the coherent 10.6 μm radiation emitted by the laser is almost completely absorbed by oxide materials, compared with 1 to 2% absorption of the output of an arc lamp. Furthermore, the relatively small diameter and divergence of a laser beam permit the use of a relatively simple and long focal length optical system for directing and focusing the radiation on to the charge rod. The optical system can therefore be positioned remote from the hot regions of the crystal growth system which eliminates problems due to distortion and allows afterheaters to be readily accommodated. In common with other thermal imaging systems the gas laser represents a clean source of heat which can be used in a wide range of atmospheres.

2. Experimental Details

2.1. The Laser System

Two 10 m long AC-energised CO_2-N_2-He lasers supplied by Ferranti Ltd are used in the present work. The output power of each laser is continuous and can be varied within the range 50 to 400 watts. The total output power of the lasers has been measured using flow calorimeters which completely intercept the primary beam, and it has been found that the power is constant to ± 1% over periods of 0.5 h.

During crystal growth the power output of each laser is continuously monitored by a stationary tungsten wire grid placed across each beam, which intercepts 1% of the beam area. The change in resistance of the grid due to heating by the laser is measured and gross changes in beam power can be corrected by manual alteration of the energising voltage to the lasers.

2.2. The Optical System

The layout of the lasers and the optical system used to focus the laser beams onto each side of an oxide charge rod is illustrated in fig. 1. Plane mirrors are used to direct the beams onto concave mirrors ($f = 50$ cm) which are positioned to give a final spot size of 1 to 2 mm diameter at the surface of the floating zone. At full laser power, this corresponds to an incident power density of 50 kW cm^{-2}. All the mirrors are front-aluminised, water-cooled and positioned on a remotely controlled gimbal mounting to allow precise positioning of the focused beams. Ideally the two beams should impinge upon the charge 180° apart in order to preserve thermal symmetry, but such a configuration allows any radiation which is not intercepted by the floating zone to pass as a diverging beam onto the opposing concave mirror with consequent damage to parts of the apparatus which intercept this beam. In practice, this possibility is eliminated by offsetting the two beams 5° from the 180° position.

In addition, some black-body radiation from the molten zone is reflected back along the optical system onto the water-cooled germanium exit windows of the laser, but this is minimised by the long focal length optics.

2.3. Crystal Growth

The arrangement of the crystal growth furnace with respect to the laser and optical systems is also shown in fig. 1. The oxide charge rod is held in the chucks of a standard, vertical floating-zone apparatus and is surrounded by an auxiliary resistance furnace which contains three small-diameter ports, two of which admit the laser beams whilst the third allows the operator to view the molten zone. The furnace is wound with either Pt-10% Rh (maximum operating temperature 1700° C) or Ir-40% Rh (maximum operating temperature 2000° C) and has three main functions. These are, firstly, to raise the ambient temperature, thereby ensuring the most efficient use of the superimposed laser heating; secondly, to reduce the melt temperature gradients in order to minimise crystal cracking; thirdly, to provide an incorporated annealing facility subsequent to growth.

Cylindrical charge rods, 0.5 to 0.7 cm diameter and up to 10 cm long can be prepared by placing the dried powders (> 99.9% purity) in a thin-walled rubber tube which is subsequently hydrostatically pressed to 3500 kg cm^{-2}. Sintering at temperatures up to 1500° C produces straight rods which have 70% of the theoretical density. When the density of the powder is very low (e.g. MgO, density = 0.6), the rods often break during the pressing process. This difficulty is eliminated by sealing the rubber tube containing the powder under vacuum prior to pressing.

In order to initiate crystal growth, two rods are employed. These are placed in the chucks of the floating-zone apparatus and positioned with their ends approximately 0.1 cm apart. The laser beams are deflected independently to melt the mating ends of the charge rods which are synchronously rotated (5 to 10 rpm) in the same direction. As heat is conducted along the rods from the molten tips, they expand to join and form a stable molten zone. At this stage, the laser beams are deflected back to the original position where they impinge upon the molten zone at the same level. The expansion effect produces severe buckling or fracture when efforts are made to melt a zone within a single charge rod. Once a molten zone is established, crystal growth is achieved by traversing the rod downwards through the beams. Typical zone lengths were 0.5 to 0.7 cm for a 0.5 cm diameter

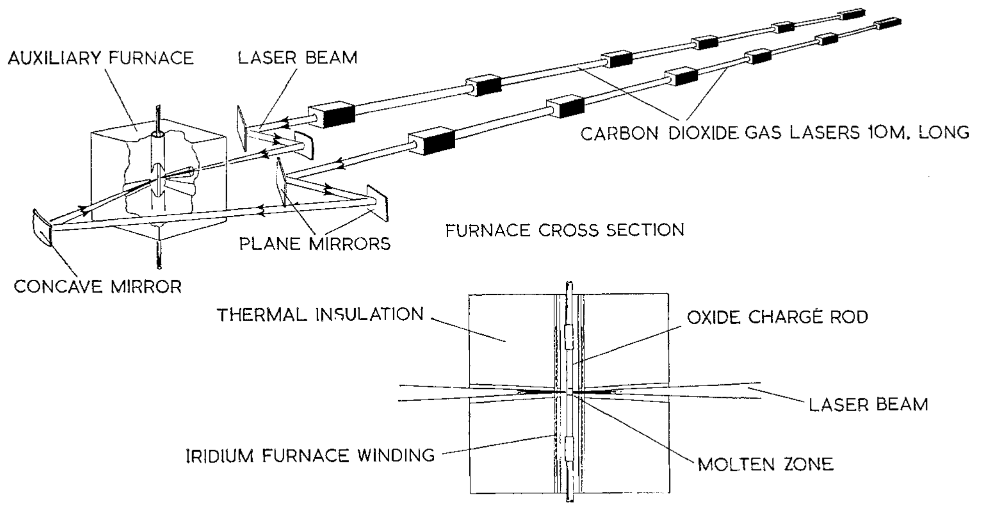


Figure 1 A schematic representation of the combined laser, optical and crystal growth system

rod. Seeded growth is made possible by replacing the lower charge rod with a section of single crystal material. The ambient is controlled by gas flowing in at the base and out through the laser beam and viewing ports of the auxiliary furnace.

3. Results and Discussion

3.1. Crystalline Materials

In order to determine the limitations of laser heating as applied to oxide crystal growth, materials with a range of melting points (2000 to 2450° C) and properties have been studied. The results, listed in table I, show that one of the major problems is evaporation of material from the molten zone. For a given material, the rate of evaporation depends markedly upon the power density in the focused beam, which is controlled by the power supplied to the laser, and the diameter of the beam incident upon the specimen. For laser beam diameters of 1 mm or less, all the materials investigated show some tendency to evaporate at their melting point. Table I lists the results obtained for beam diameters of 1 to 2 mm at the minimum power level required to melt the materials in air with the auxiliary furnace standardised at a temperature of 1700° C. Under these conditions, stable molten zones of $CaZrO_3$, Y_2O_3, $MgAl_2O_4$ and Al_2O_3 have been formed, and single crystals of these materials (fig. 2) 5 mm in diameter and several centimetres long have been readily obtained by passing the charge rod through the laser beams at rates of 1 to 3 cm h^{-1}. Straight cylindrical crystals have been grown using synchronous rotation for the seed and charge rods. Under the same conditions, less stable molten zones can be formed in rods of La_2O_3, Nd_2O_3 and Gd_2O_3. These materials either evaporate or dissociate. However, the rate of loss of material is sufficiently low to allow a zone to be passed through the material, although polycrystalline rather than single crystal rods are then produced. The other three materials studied, CaO, CeO_2 and MgO are known to be volatile, and evaporated with no evidence of melt formation. The rate of evaporation is minimised by using a static rather than a flowing gas ambient.

TABLE I

Compound	MP, °C	Vaporisation during growth	Crystalline state
Y_2O_3	2450	v. slight	single crystal
Al_2O_3	2050	none	single crystal
$MgAl_2O_4$	2105	none	single crystal
$CaZrO_3$	2375	none	single crystal
Nd_2O_3	2250	moderate	polycrystal
Gd_2O_3	2350	slight	polycrystal
La_2O_3	2315	moderate	polycrystal
CeO_2	2600	complete	no melt formed
CaO	2580	complete	no melt formed
MgO	2800	complete	no melt formed

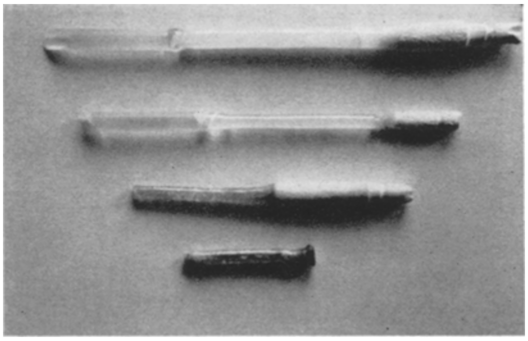
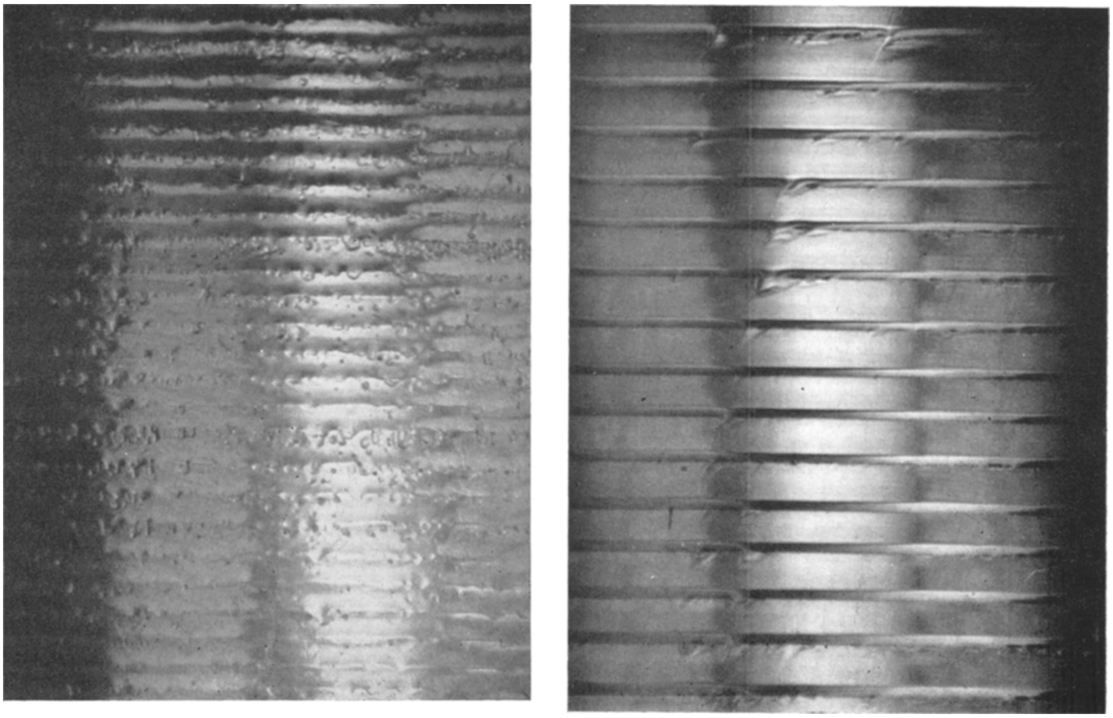


Figure 2 Crystals grown using gas lasers as the heat source in the floating-zone recrystallisation apparatus Top, $MgAl_2O_4$; second, Al_2O_3; third, Y_2O_3; bottom, $CaZrO_3$ (× 0.4).

3.2. Crystal Quality

Optically transparent crystals of Y_2O_3, $CaZrO_3$, $MgAl_2O_4$, Al_2O_3 and Nd_2O_3 have been produced. The crystals show the principal features of float-zoned crystals. For instance, they are generally strained due to the small melt volume and associated steep temperature gradients which subject the growing and cooling crystal to severe thermal stresses. In Y_2O_3 and $CaZrO_3$ crystals this problem is particularly severe because of the large difference in temperature between the melting point of the material and the auxiliary furnace. As a consequence, these materials quite frequently crack, whereas lower melting point materials such as Al_2O_3, $MgAl_2O_4$ and Nd_2O_3 are crack-free but have high dislocation densities (10^6 cm^{-2}) compared with Czochralski-grown crystals (10^3 cm^{-2}). Furthermore, the crystal surface, fig. 3, shows the growth rate fluctuations (revealed as a helical thread-like marking) which occur due to the crystal being rotated through an asymmetric thermal field. The spacing between the fluctuations corresponds to one revolution of the crystal. At growth rates of less than 3 cm h^{-1} the surface of the crystal appears to be slightly thermally etched or locally remelted by the laser beam as



(a) (b)

Figure 3 Surface structure of Al_2O_3 single crystals rotated at 7.7 rpm. (a) growth rate 3.0 cm h^{-1}; (b) growth rate 5.1 cm h^{-1} (× 55).

shown in fig. 3a. At higher growth rates, the crystal surface is free from such defects and is typified by fig. 3b. The transparency of the crystal interior is unaffected by the surface damage.

Application of the technique to zone-refining is of particular interest because Y_2O_3, Al_2O_3 and Nd_2O_3 are the basic components of the laser material $Nd^{3+}/Y_3Al_5O_{12}$ and hitherto, have been entirely dependent upon chemical methods for their purification. In addition to purification, the passage of a zone through the primary components allows each oxide to be individually assessed for the presence of scattering particles e.g. impurity precipitates which impair the optical perfection of the mixed oxide crystal. The growth of crystalline Nd_2O_3 illustrates the advantage of working at atmospheric pressure. In a cold-cathode electron beam apparatus, Nd_2O_3 is highly volatile and does not form a molten zone [7]. This material is also hygroscopic and at room temperatures requires the presence of a drying agent in order to maintain the transparent crystalline form.

3.3. Laser Beam Power Control

The problems associated with stabilising high-power laser beams during the time periods needed to grow crystals longer than 5 cm have not been fully solved.

There are two sources of beam power instability, firstly, variations in energising voltage and secondly, changes in the gain of the laser cavity caused by thermal and mechanical movement of the cavity window and mirror. A simple control method is to vary the energising voltage in response to a signal which is proportional to the beam power, possibly using a servomechanism. Such a system automatically compensates for any variation in gain within the laser cavity.

The main problem is to obtain a reliable signal which is proportional to the beam power. The possibility of briefly intercepting the whole beam is not practicable because the short period of time when no heat falls upon the molten zone causes crystal growth-rate fluctuations which impair the crystal quality. Continuous sampling of a small fraction of the beam (1 %) offers a more satisfactory solution but the tungsten wire grid used here is unreliable over time periods greater than 3 h and is also sensitive to convective effects in the surrounding ambient. At the present time, a rotating blade reflector is being developed to sample 1% of the total beam cross-section. Such a device automatically accounts for changes in the laser mode pattern, is independent of effects due to convection and ensures that the detecting device does not measure black-body radiation from the molten zone in addition to the laser beam power.

4. Conclusions

The present work clearly establishes that single crystals of high melting point oxides and mixed oxides can be grown using gas lasers as a heat source in a floating-zone recrystallisation apparatus. The crystals produced are often strained but the high temperatures attainable permit the growth of materials which cannot readily be produced in single crystal form using existing techniques. One important use of the technique is to zone-refine materials which have previously relied entirely upon chemical methods for purification because of their high melting point. Future developments envisaged are firstly, the provision of a pressurised environment to further restrict evaporation; secondly, the development of a reliable power-monitoring system which can be used directly to control laser beam power thereby eliminating manual operation; thirdly, the adaptation of laser heating to Czochralski-growth with its inherently lower thermal gradients which minimise strain in the crystals produced.

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