Infrared Laser-Assisted Zone Refining of Inorganic Materials

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This paper presents purification and crystallization of inorganic materials by laser zone refining (LZR), i.e., floating zone melting assisted by a high power infrared laser. The LZR heating system was composed of a Nd: YAG laser as a heat source, an optical fiber for laser beam transmission, and a focusing system. To determine LZR purification capabilities, 5 mm zinc rods were melted and Pb impurity segregation was observed after refining the zinc rods. For the crystallization test, green bodies of 0.2 μm α-Al2O3 fine powder were fused, and optically transparent single crystals were obtained. The LZR technique was found to be useful in the refining of inorganic materials.

Key-words: Laser assisted, Zone refining, Zinc, Alumina, Single crystal growth, Melting

1. Introduction

High purification and single crystal growth of inorganic materials have been performed by both the Czochralski method and a floating zone melting technique (FZ). The FZ has been shown to be superior in preventing crucible surface contamination, with several kinds of heat sources being used to form the molten zone. Materials with a low melting point have been refined by the FZ using electron beams and radio-frequency induction.

Recently, an optical zone refining process has been developed for crystallization of oxides and chalcogenides having melting points above 2000°C. Kitazawa and Kaneko et al. devised an infrared (IR) heating system using a Xe-arc-image furnace equipped with ellipsoidal mirrors. A floating zone technique using a CO2-N2-He laser heat source was devised by Gasson et al., whereas a laser process with a cw CO2 laser was developed by Feigelson et al. A laser heating system is advantageous because it can control the molten zone length, and also utilize several types of irradiation systems.

This paper examines inorganic material purification and crystallization by the laser zone refining (LZR) method using a Nd : YAG laser heat source equipped with an optical fiber.

2. Experimental

Figure 1 illustrates the experimental LZR set up. A cw Nd : YAG laser (NEC-SL116), with a 200 W output power variation was used as a heat source, with the silicon fiber optical transmitting 89.4% of IR light at λ = 1.06 μm. An optical system focused the laser beam as shown in Fig. 1.

A rod shaped test specimen attached to a translation apparatus was irradiated by the laser beam on one side. Once the specimen formed a molten zone, it was translated either upward or downward while rotating at a constant speed. The rotational speed and moving rate of the specimen were respectively from 0.04–42 rpm and 0.33–2 mm/min. A 5 mm zinc rod (m.p. = 420°C) was melted and used for the purification tests, with feed specimen purity being 99.99%.

Al2O3 green bodies in the form of 0.2 μm α-Al2O3 powder molded by a cold isostatic pressing were used for the crystallization tests. The molded Al2O3 density was 99% of the true density, and a green body in the shape of a rectangular prism-like rod (base of 2 mm × 2 mm) was melted. The Al2O3 green body was melted in the air, whereas the Zn rod was melted in Ar gas flowing in order to avoid its oxidation.

The Zn impurity concentration was analyzed by induced coupled plasma spectroscopy (ICP), and the melted Al2O3 crystalline structure was examined by X-ray diffraction analysis.

Fig. 1. Experimental apparatus for laser zone refining.
3. Results and discussion

3.1 Metal purification

The effects of moving direction of the specimen on the molten zone’s shape and state were tested before studying LZR characteristics. With upward moving, the molten zone was unstable and the melted metal dripped, therefore, the specimen was moved downward in the refining experiments.

Figure 2 shows the distribution of Pb and Cu impurity concentration in a melted Zn rod. The ratio of impurity concentration before \((C_o)\) and after \((C)\) melting, \(C/C_o\), is plotted as a function of moving distance \(x\). The rod was refined twice at a rate of 0.213 mm/s and a rotational speed of 5.19 rpm. No variation in weight was detected between the feed and melted specimens, thus, Zn oxidation and vaporization are considered negligible. The variation coefficients in the Cu and Pb ICP analysis were respectively 1-4% and 10-30%, with the \(C_o\) values of Cu and Pb being respectively 6.6 ppm and 25 ppm.

The concentration distribution after LZR indicates that the Pb impurity was condensed at the end of the Zn rod as shown in Fig. 2. The distribution coefficient \(k\) of Pb was calculated as 0.35 from the experimental results. On the other hand, no Cu concentration variation was detected and the \(k\) value of Cu in Zn was found to be near unity. The variation of \(k\) values of Pb and Cu is considered due to that Pb ion (Pb\(^{2+}\)) is 1.5 times as large as Zn\(^{2+}\) one whereas Cu\(^{2+}\) radius is nearly equal to Zn\(^{2+}\). Hence the LZR method was found to be applicable to metal purification.

3.2 Crystallization of alumina

Figure 3 shows an as-grown Al\(_2\)O\(_3\). Optically transparent Al\(_2\)O\(_3\) was obtained at a moving rate less than 0.5 mm/min. X-ray diffraction analysis using a back Laue technique showed that the Al\(_2\)O\(_3\) was a single crystal, thus, the present LZR system can produce a single crystal growth of oxide.

Contrastingly, optical transparency could not be obtained when a coarse 5 μm Al\(_2\)O\(_3\) powder mold was melted, i.e., the density of molded Al\(_2\)O\(_3\) was about 90% of the true density. After melting, pores were observed in the cross section of solidified body. In the finer powder molding, however, pores could not be observed, resulting in a highly transparent rod being obtained as shown in Fig. 3. It was found that a decline in transmission was caused by pores that remained in the body.

4. Conclusion

A laser zone melting system using a cw Nd:YAG laser equipped with an optical fiber was developed, and the ability to refine inorganic materials has been examined. The results show that the laser system is useful for both metal purification and single crystal growth of oxides.

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