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Growth of platinum fibers using the micro-pulling-down method

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ABSTRACT

Platinum (Pt) crystalline fibers were grown from the melt by the micro-pulling-down (μ-PD) method using the ZrO_2 ceramics crucible. The diameter of the grown Pt fiber was controlled by the ϕ1 mm outlet made at the bottom of the crucible and the Pt fiber of 0.95 ± 0.03 mm in diameter and over 5 m in length was obtained at 10 mm/min pulling-down rate. In addition, the Pt fiber was grown at 1–110 mm/min pulling rates while the liquid-solid interface reached the bottom of the crucible and the crystal growth became unstable at 120 mm/min pulling rate. Few grain boundaries were observed in the scanning electron microscopy image of the Pt fibers and there were some spots with high intensity in the pole figures.

1. Introduction

The industrially available noble metals such as Platinum (Pt) and Iridium (Ir) have been applied in various fields due to high oxidation resistance, high melting point and catalytic property. In applications, these metals are used in various configurations. For example, electrodes of an Ir-alloy spark plugs in car engines are utilized in the shape of needle to explode gaseous fuel efficiently. In addition, Pt wires have been applied in the thermocouples used at high temperature and these fiber-shaped products have been used in many applications. However, it is difficult to make such fibers directly, and various forming processes including wiredrawing and swaging are practiced. Formation of a wire-like product from initial bulk ingot increases manufacturing cost. Especially in the case of the noble metals, processing loss of a starting material has an enormous effect on the product price.

In the past, we have developed various functional single crystals with help of the micro-pulling-down (μ-PD) method [1,2]. In this technique, the melt container (the crucible) is equipped with one or several orifices on its bottom. The melt passes through the orifice(s) and solidifies on the seed material positioned just below the orifice(s). The single crystal growth is established due to continuous displacement of the seed in downward direction together with appropriate control of temperature gradient conditions. In addition, the μ-PD method is also suitable for the growth of shaped crystals when the crucible is produced with a die of appropriate shape configuration. Number of shape-controlled oxide [3] and halide [4] single crystals, including fiber-shaped single crystals [5–7], have been developed using metal and graphite crucibles. Growth of the non-metallic shape-controlled single crystals by the μ-PD method demonstrated that cost of the post-growth forming of such materials can be reduced considerably. Therefore, development of the growth process that is suitable for the production of the shape-controlled noble metal fibers by the μ-PD method was initiated. To achieve this goal, a ZrO_2 ceramics crucible suitable for high temperature crystal growth applications was developed. As a result, growth of Ir fiber from the melt by the μ-PD method using the ZrO_2 crucible was demonstrated [8]. In this paper, we developed the growth of the shape-controlled Pt fibers by the μ-PD method and examined their local structure and the crystal orientation.

2. Experimental procedure

Pt fibers were grown by the μ-PD method using high-frequency (HF) induction heating and a pinch roller. High purity Pt ingots (4N) were used as a starting material and they were set into a ZrO_2 crucible with a ϕ1 mm opening at the bottom. The ingots were directly heated by the HF induction coil up to the melting point of Pt (1768 °C). After the ingots were completely melted, a commercial Pt wire of ϕ0.95 mm in diameter was immersed into the opening and brought into physical contact with the melt in the crucible. Then, the Pt fiber was grown from the melt by pulling-down the melt using the Pt seed wire under N_2 flow. The growth of the Pt fiber was observed during the growth through the holes of an after-heater and an insulator by a Charge Coupled Device

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(CCD) camera. After the growth of the fiber, the melt was cooled to room temperature for 2 h. Two Pt fibers were grown at different growth rates to understand an effect of the growth rate on the internal structure of the grown fibers. At first, a Pt fiber was grown at constant growth rate of 10 mm/min and the growth was continued as long as the fiber was grown. Secondary, the growth rate of the Pt fiber was sped up starting from 1 mm/min.

The as-grown Pt fibers were cut to prepare specimens for observation of the local structure and characterization using X-rays. The cut specimens were polished parallel and perpendicular to the growth direction using sandpapers and lapping film sheets. In addition, the surfaces of the polished specimens were treated by Cross section polisher (CP) (JEOL, IB-09020CP) with Ar^+ ion under 5 kV accelerating voltage to observe domain structures. Local structures on the polished and the CP treated surfaces of the fibers were observed by scanning electron microscope (SEM) (Hitachi S-3400N). Pole figures and X-ray rocking curve (XRC) on the surfaces perpendicular to the growth direction were measured to identify the crystal orientation and the crystallinity of the fiber using X-ray diffractometer (Bruker, D8 DISCOVERY). Pole figures were collected for reflections from (111) and (200) planes in the tilt and rotation angle range of ψ=0–80° and ϕ =0–360°. In the XRC measurement, ω scan was carried out for reflection from (111) plane.

3. Result and discussion

Fig. 1 illustrates the Pt fiber grown by the μ-PD method at 10 mm/min growth rate and the bottom of the crucible as it was observed during the crystal growth. When the growth was performed, the liquid-solid interface was established in the opening of the crucible and therefore, the diameter of the grown Pt wire was controlled by the diameter of the opening. The position of the liquid-solid interface was established by careful adjustment the temperature gradient and the growth rate. When these two parameters were well adapted, the growth of the fibers was highly stable from the initial part to the end part. As a result, the length of the grown fiber exceeded 5 m and no fluctuations of its diameter were observed with the naked eye. The diameter measured by a micrometer was 0.95 ± 0.03 mm from the initial part to 5 m position. On the other hand, at the distance exceeding 5 m from the growth initiation, the diameter of the Pt fiber gradually reduced from 0.93 to 0.87 mm. This diameter reduction was associated with insufficient supply of the Pt melt from the interior part of the crucible to its outlet. Finally, the growth of the Pt fiber was finished by breaking the fiber as a result of the shortage of the melt remained in the crucible.

In addition, a Pt fiber was grown under the same growth conditions except for the growth rate. During the growth, the pulling-down rate was gradually increased from 1 mm/min to 120 mm/min at the distance of 100 mm. In the growth range of 1–110 mm/min, the growth was visually stable and the fiber with approximately 1 mm diameter was grown. However, the diameter of the grown fiber began to change suddenly at 120 mm/min growth rate and the growth became unstable. Based on these observations, it was suggested that the liquid-solid interface was generally located within the opening channel of the crucible when moderate (1–110 mm/min) pulling rates were applied. Alternatively, the interface was displaced in downward direction to outer bottom surface of the crucible resulting failure of the meniscus stability at 120 mm/min pulling-down rate. Thus, suitable growth rate and temperature gradient are considered to be critical parameters responsible for the stable growth of the Pt fiber. Some small pits were observed on the surface of the Pt fiber and they were considered to be attributable to the gas dissolved in the Pt melt or the gas from the crucible. However, exact mechanism of formation of the pits is not clear now.

The local structures of the grown fibers and the commercial Pt wire were observed by the SEM and such images are shown in Fig. 2. Large arrows in Fig. 2 are growth directions (Fig. 2(a) and (b)) of the fiber produced by the μ-PD method and longitudinal direction of the commercial wire (Fig. 2(c)), respectively. Fig. 2 shows the SEM images of the mechanically polished and the CP treated surfaces parallel to the growth direction. The obtained Pt fiber had constant diameter and the diameter was slightly smaller than 1 mm. Domain structure of the grown Pt fiber could not be observed in the images on the mechanically polished surfaces. Therefore, the surface was treated by the CP and as a result the grain boundaries appeared in the SEM images of the CP treated surface. The grains had millimeter-scale dimensions and just one or two grain boundaries were detected in the Pt specimen with 5 mm length. The local structure of the commercial Pt wire was also inspected for its comparison with that illustrated in Fig. 2(b). According to SEM, the mechanically polished surface of the commercial Pt wire was very similar to that of the Pt fiber grown by the μ-PD method. After the CP treatment, the surface of the commercial Pt wire was modified according to the image with the line structure as it is demonstrated in the Fig. 2(c). According to the SEM image, there were many lines oriented parallel to the long direction of the CP treated surface of the commercial Pt wire. The origin of the lines is not clear now. Nevertheless, the lines are considered to be attributable to the

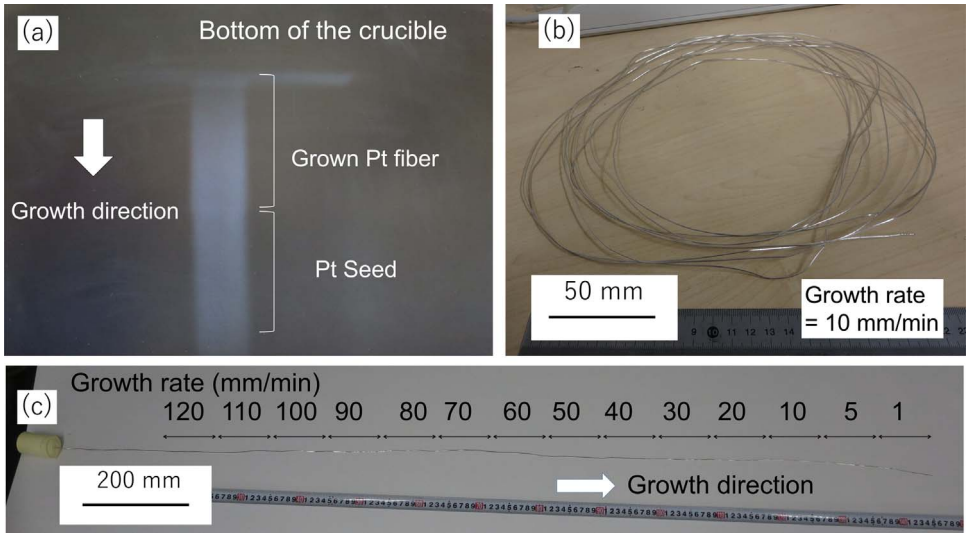

Fig. 1. (a) View of the growing fiber and the bottom of the crucible during the crystal growth. (b) Pt fiber grown at 10 mm/min pulling-down rate. (c) Pt fiber grown at various pulling-down rates (1~120 mm/min).