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The characteristics of single crystal bismuth wires produced by the Ohno continuous casting process

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Bismuth wires approximately 2 mm in diameter were produced by the heated mould Ohno Continuous Casting process and their mechanical characteristics evaluated. It was found that cast wires produced under all speed conditions from 30 to 170 mm min^{-1} were single crystals. Cast wires with an angle between the cleavage plane and wire axis of less than about 40° were significantly more ductile than those with an angle of over 57°. The former could be bent repeatedly before fracture occurred whereas the latter fractured after only a single bend. It was also found that the bismuth wires with a cleavage angle of less than 45°, exhibited tensile elongations up to about 130%. © *1999 Kluwer Academic Publishers*

1. Introduction

Small diameter bismuth and bismuth-bearing alloy wires are required for applications such as thermal fuses, solders, and metallurgical additives. However, due to the intrinsic characteristics of bismuth (fragility, brittleness, and friability [1]), it is difficult to produce bismuth and high bismuth-bearing alloy wires 1–3 mm in diameter by extrusion. Although, the Ohno continuous casting method may serve as an alternative approach, the conventional continuous casting process in which the liquid metal solidifies within the water-cooled mould is not a viable method. Since bismuth wire could easily break within the mould because of mould-strand friction enhanced by the expansion of bismuth upon solidification. Thus, in previous work [2], the feasibility of producing bismuth wires by a different continuous casting method which uses a heated mould was examined and it was found that wires with 0.5–2 mm diameter could be produced. The general concept of this heated mould process, which is known as Ohno continuous casting (OCC) [3], is shown schematically in Fig. 1. Molten metal is introduced continuously into an externally heated mould and heat extraction from the cast product is carried out using the cooling device located near the mould exit. Thus, unidirectional solidification occurs along the casting direction at or near the mould exit. As a result, mould-strand friction is eliminated and this permits the production of small diameter net-shape cast products without breakage. When solidification occurs at the mould exit, the effect of expansion of bismuth upon solidification diminishes, so the casting of small bismuth wire is possible. The objective of the present study is to characterize cast bismuth wires produced by this continuous casting method.

2. Experimental aspects

Fig. 2 shows a schematic diagram of the melting and casting arrangement designed to apply the principle of the heated mould continuous casting process to the production of a small diameter wire. It consists of a graphite melting crucible, a mould constructed out of a 130 mm long and 30 mm diameter graphite rod, a cooling device, a support tube for minimizing the mechanical instability, and pinch rolls for withdrawal of cast wires.

Approximately 4.5 kg of a bismuth ingot of 99.99% purity was melted in the crucible, with temperature maintained at 320 °C, and fed into the mould continuously through a runner by lowering a level control device into the melt. The mould, wound with a single layer of nichrome wire of 0.8 mm diameter and secured with alumina cement, has a rectangular opening (10 mm × 50 mm) which serves as a tundish and also makes it easy to maintain an appropriate metal head by simply observing the metal surface level in the tundish during casting. At one end of the tundish wall, there is a 2 mm diameter, 3 mm long channel, through which the liquid metal exits into the cooling zone, to produce wires. The maximum metal head above the channel was approximately 2–3 mm. The control thermocouple, positioned close to the channel, monitored the melt temperature in the tundish which was maintained at about 274–286 °C. Fig. 3 shows a measured temperature profile within the melt in the tundish.

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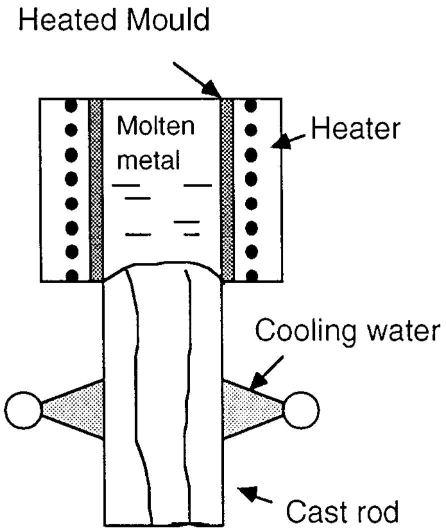

Figure 1 Schematic diagram of the concept of the heated mould continuous casting process.

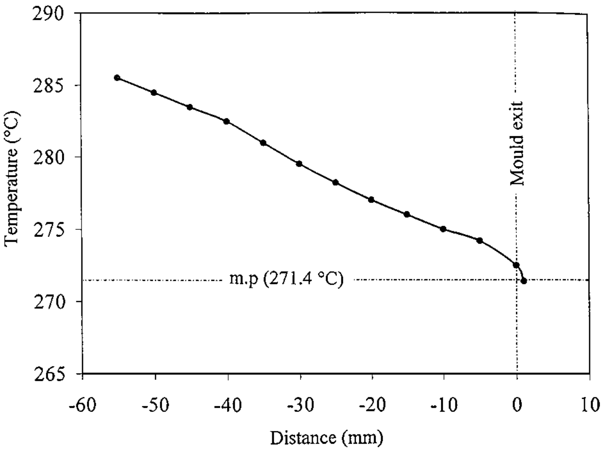

Figure 3 The temperature profile within the melt in the tundish during casting.

Cooling of the wire was obtained with two columns of spray water located close to the channel exit. The distance between the channel exit and cooling water was adjusted between 2 and 10 mm depending on the casting speed. The position of the solidification front must be located approximately within 3 mm from the mould exit to be able to cast wires of 2 mm diameter without breakout. A glass tube 250 mm long and 4 mm in inner diameter, provided support for the cast strand in order to improve mechanical stability. Approximately 10 mm of the top half of the glass-tube was removed so that the column of cooling water could fall directly onto the remaining portion of the tube wall, allowing the water to enter the tube thus ensuring good contact between the cast strand and cooling water. The amount of cooling water used was about 120 ml min^{-1}.

To start casting, a stainless steel wire 2 mm in diameter with a tapered end was inserted into the channel in order to bring the liquid metal to the exit. After ensuring good contact between the steel wire and the liquid metal, the cooling water was turned on and casting initiated by moving the pinch rolls. Wires approximately 2 mm in diameter and 1.2 m in length were produced in each casting operation with casting speeds of 30, 100, and 170 mm min^{-1}. In some instances, a seed crystal was attached to the dummy bar to produce wires with different crystal orientation. The cast wires were sectioned into an appropriate length for mechanical testing. The results were correlated with the angle between the cleavage plane and the wire axis. This angle will be referred to as the cleavage angle.

3. Results and discussion

3.1. Cast wires

3.1.1. Single crystal

Fig. 4 shows an example of a cast bismuth wire. It was found that after approximately 20 cm of casting, the wires became single crystal with casting speeds of 30, 100, and 170 mm min^{-1}. Since the nominal solidification front for these casting conditions was kept at approximately 1 mm from the mould exit and the melt temperature at the mould exit was 272.5 °C, the temperature gradient just ahead of solidification front is $\sim$1 °C mm^{-1}. Monocrystallinity was confirmed by optical microscopy or by observing the cleaved surface of the wires. Fig. 5 shows typical cleaved cross-sections

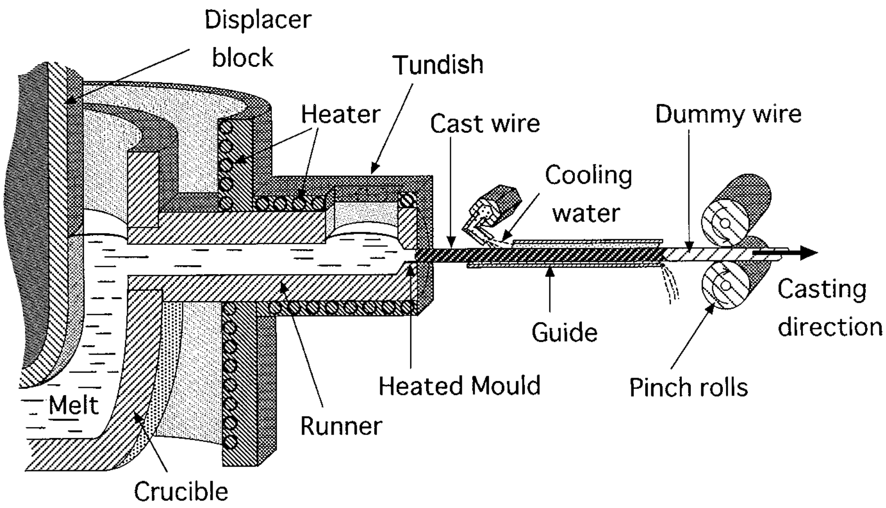

Figure 2 Schematic diagram of the experimental melting and casting arrangement.

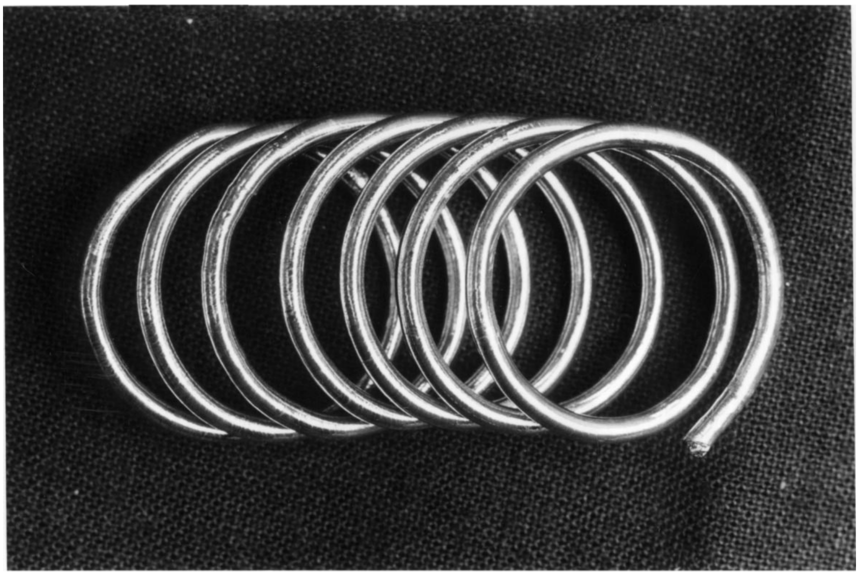

Figure 4 Example of cast bismuth wire 1.6 mm in diameter produced by the OCC process.

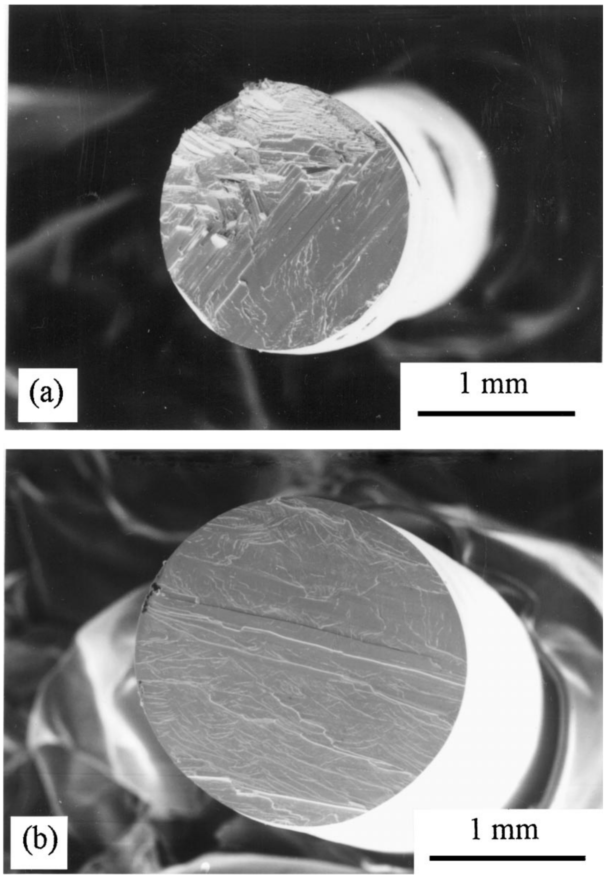

Figure 5 Cleaved surfaces of (a) polycrystal and (b) single crystal wires produced by the OCC process. Sample (a) is taken from the starting end and sample (b) 20 cm away from the starting end, of the cast wire.

of OCC samples taken from the starting end, and 20 cm away from the starting end, of the cast wire. A flat cleavage surface across the diameter of a cast wire indicates that the wire is in fact a single crystal.

3.1.2. Growth orientations

Yamamoto and Watanable [4] produced single crystal bismuth rods 5 mm in diameter using the Bridgman method with growth speeds of 0.4–21.3 mm min^{-1} and a temperature gradient of $34\,^{\circ}\text{C cm}^{-1}$. They observed that the angle between the crystal rod axis and the [111] trigonal axis tended to be greater than 70° and the most frequently observed angles were ∼80° which in this case means that the (111) plane lies almost parallel to the rod axis. Furthermore, there was no crystal with the [111] orientation in the growth axis of the rod. Vigdorovich *et al.* [5] produced single crystals of bismuth using the Czochralski method with much slower growth rates of 0.2–0.22 mm min^{-1} and reported that the predominant growth orientation of crystals was the [$\bar{1}10$] direction which accounted for 71.5% of the total products. Crystals whose growth axis was in the [100] direction amounted to 21.4%, and crystals with a growth axis close to the trigonal axis (deviation of no more than 10–12°) amounted to 7.1%. The results of Yamamoto *et al*. and Vigdorovich *et al*. indicate that different preferential growth orientations depend on the growth conditions. However, in both cases, bismuth crystals with a growth direction parallel to the [111] axis were difficult to obtain.

In the present study, the effect of casting speed on growth orientation was also examined by producing eight specimens at each casting speed of 30, 100 and 170 mm min^{-1} for a total of 24 specimens. The growth orientation was determined by electron channeling pattern (ECP) analysis. The wire specimens were mechanically and electrochemically polished prior to channeling pattern analysis. The polishing conditions were 30 V at room temperature for 5–10 s and the electrolyte was a mixed solution of 100 ml phosphoric acid, 200 ml sulfuric acid, and 200 ml distilled water. The reference channeling map for a face-centered rhombohedral crystal was not available in the literature, so an electron-channeling map was constructed. The channeling map obtained was similar to the diffraction symmetry of a FCC crystal or a diamond cubic crystal because the axial angle of the bismuth crystal (angle between edges of the rhombohedron) is 87.57° [6] which is close to the axial angle for the cubic crystal (i.e.

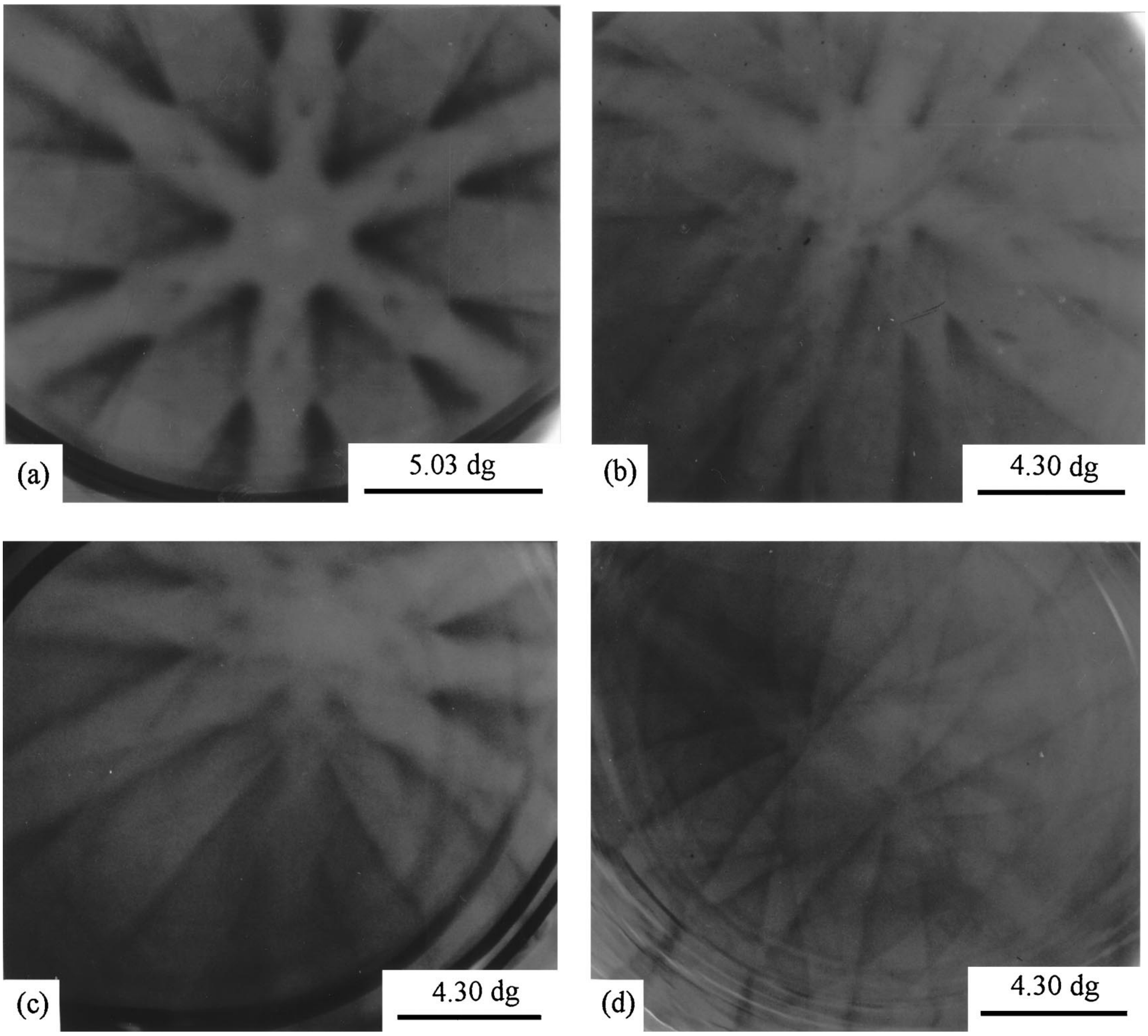

Figure 6 Electron channeling patterns of major poles of bismuth crystal: (a) (111), (b) (001), (c) (011), and (d) (012) poles obtained using a backscattering mode at 25 kV.

90°). The electron channeling patterns of major poles, which are easily identifiable with the symmetries of cubic crystals, are shown in Fig. 6. A channeling map for bismuth is shown in Fig. 7 and the growth orientations of the wires produced under different casting speeds are plotted in a schematic diagram of the channeling map as shown in Fig. 8. It is clear that with a casting speed of 30 mm min^{-1}, the growth orientation varied most widely, whereas at higher casting speeds, the orientation tended to cluster near the [111] direction. These results indicate that the [111] direction is the preferred growth orientation under higher casting speeds (e.g. 170 mm min^{-1}), confirming a generally reported preferred-orientation for growth of bismuth grains solidified normal to the cold surface of the casting mould [7]. However, with lower casting speeds, crystals with growth orientations other than the [111] direction can be produced.

3.2. Ductility of cast wire

Polycrystalline bismuth aggregate is brittle despite its softness. For example, the teardrop shaped grains produced by pouring molten bismuth into water broke easily with slight bending. Although the same is also true of many of the single crystal bismuth wires produced by the OCC process, it was found that some wires were remarkably soft and ductile and could be bent in a U-shape or by 90° repeatedly before fracture occurred. They were also easily wound into a coil as shown previously in Fig. 4. However, wires which produce clear audible clicks when bent were less ductile than those with faint clicks or no clicking sounds. The more brittle wires cleaved after several bendings or sometimes after only a single bend. This suggests that bismuth single crystal wires have marked deformation anisotropy. Depending on the growth orientation, bismuth wire appears to deform either by slip or twinning before fracture occurs. It is known that bismuth crystals cleave along the (111) plane at room temperature. This was confirmed by observing the orientation etch pits on the cleaved surface by SEM and optical microscopy. Fig. 9 shows equilateral triangular etch-pits on the cleaved surface confirming that the exposed surface is the (111) plane. The electron channeling pattern obtained on the same cleavage plane also showed characteristics of the

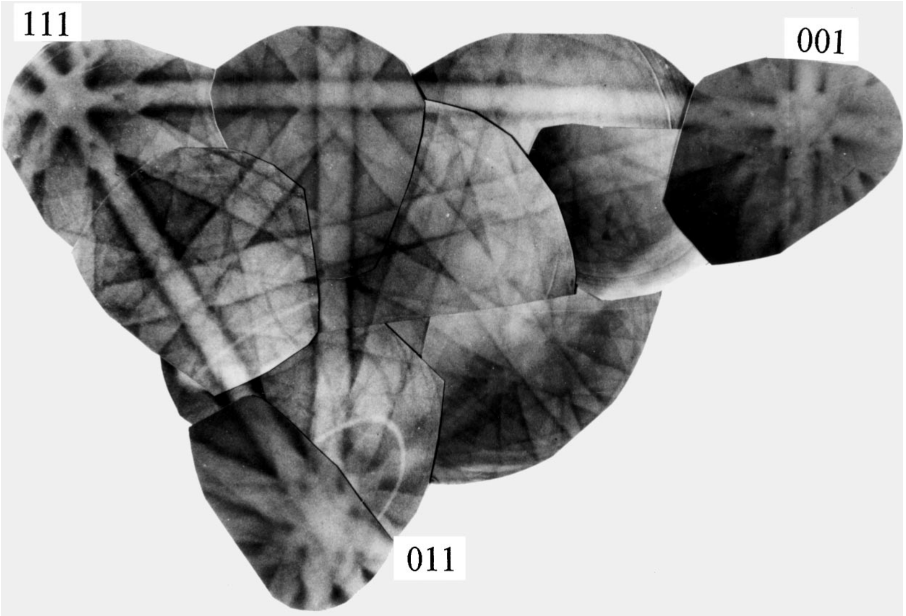

Figure 7 Electron channeling map for bismuth crystal.

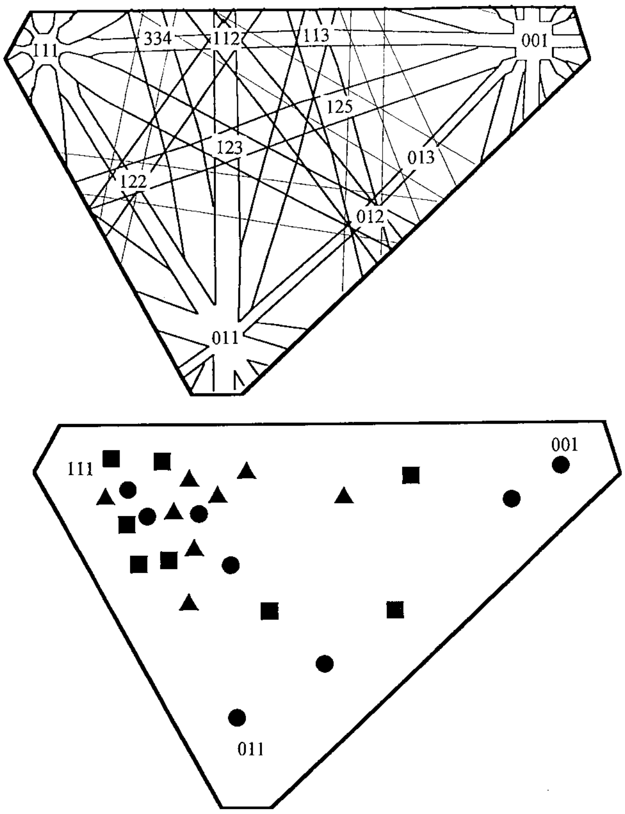

Figure 8 The effects of casting speed on crystal growth orientation. The casting speeds: (●) 30, (■) 100, and (▲) 170 mm min^{-1}.

diffraction band symmetry of a ⟨111⟩ crystal orientation (Fig. 6a).

To observe the degree of ductility as a function of crystal orientation, wire specimens were subjected to a simple 90°-bend test until fracture occurred. Since cast bismuth wires were found to fracture parallel to the (111) plane, the number of bends required for fracture of the wire was correlated with the cleavage angles in reference to the wire axis. The results are shown in Fig. 10. It is clear that the flexibility varies significantly

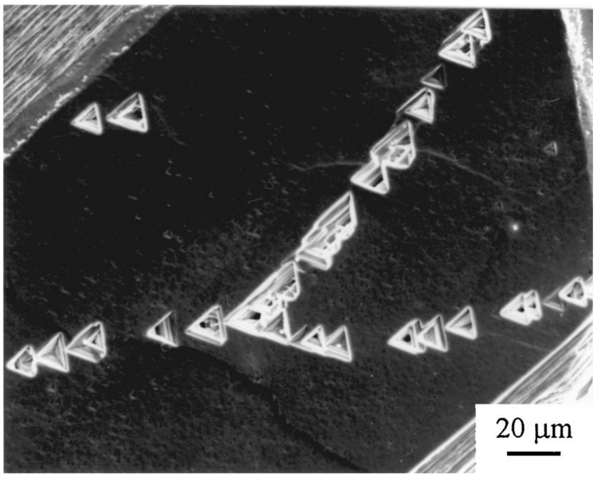

Figure 9 Equilateral triangular etch-pits on the cleaved surface indicating that the exposed surface is the (111) plane.

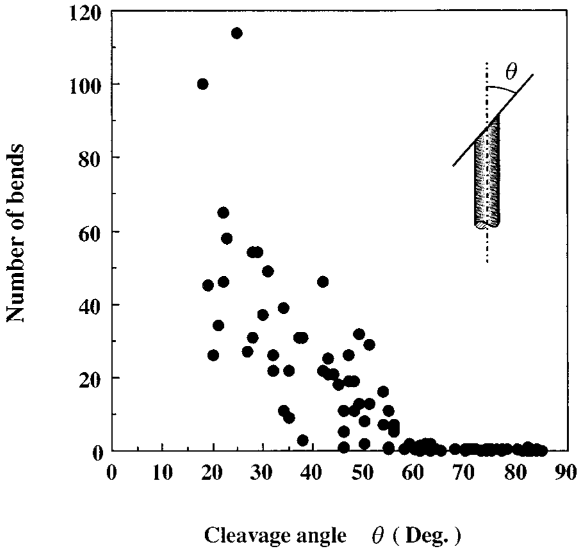

Figure 10 Number of bends required for wire fracture versus cleavage angle.

with orientation. Wires with a cleavage plane closer to perpendicular to the wire axis (e.g. a cleavage angle of more than about 57°) exhibited no bending properties whereas those with a cleavage angle below 57° showed ductility which increased as the angle became smaller. Wires with a cleavage angle less than 30° showed significant ductility. Since the (111) plane is both the slip and the cleavage plane, the (111) plane, which lies normal to the direction of the applied stress, causes cleavage fracture more easily compared to the (111) plane lying closer to the direction of stress. Thus, with lower angles more applied stress will be resolved along the slip plane promoting slip. Since these aspects can be expressed in terms of tensile elongation and cleavage angle, tensile tests were performed using specimens with known cleavage angles based on information from bend tests. For this purpose, specimens with a wide range of cleavage angles were selected. The tests were conducted with a gage length of 50 mm and a crosshead speed of 1 mm min^{-1}. This corresponds to an initial strain rate of $3.3 \times 10^{-4}\ \text{s}^{-1}$.

Fig. 11 shows typical stress-strain curves for specimens known to have a cleavage angle of 81° and 29°. Fig. 12 shows the elongation values as a function of the cleavage angle of the specimens tested. It is clear that there was little deformation in specimens having the (111) plane positioned closer to perpendicular to the wire axis. The stress-strain curve exhibited jagged irregularities (Fig. 11a), indicating that the specimen deformed by twinning. On the other hand, specimens with lower cleavage angles showed remarkable elongation, sometimes as much as 130%.

Despite the general belief that bismuth is brittle, it is evident that single crystal bismuth wires can be strained significantly if the crystal orientation is aligned appropriately with the direction of applied stress. For example, angles between (001) and (111) poles and also between (011) and (111) poles are 56.38° and 36.97°, respectively [6]. Thus, if the cast wire has the [001] growth orientation, the angle between the wire axis and the (111) plane will be approximately 33° and this wire will exhibit good ductility with above 100% tensile elongation. Cast wires with [011] orientation, which produce a cleavage angle of approximately 53°, would have approximately 30% elongation. On the other hand, for wires with growth orientations in the [211] or [311] directions, the cleavage angle is approximately 69° or 59°, respectively, and these wires will exhibit brittle behaviour when bent or strained in tension.

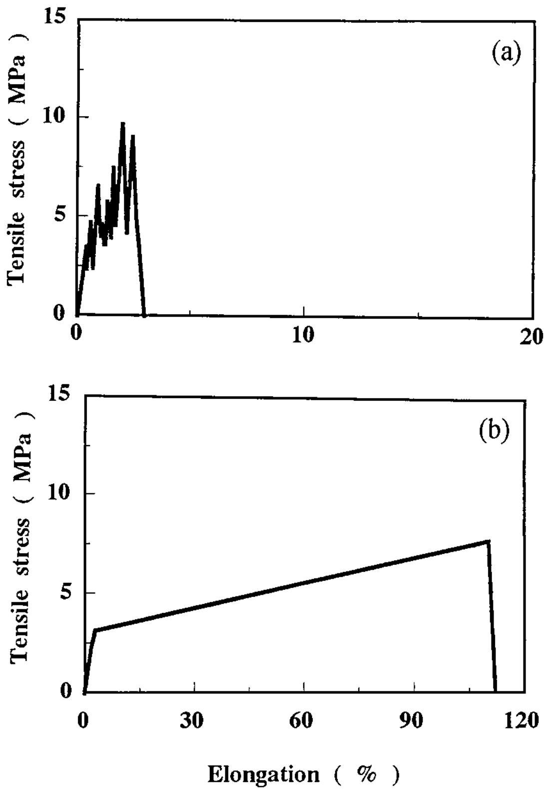

Figure 11 Typical stress-strain curves for specimens with a cleavage angle of (a) 81° and (b) 29°. The initial strain rate was $3.3 \times 10^{-4}\ \text{s}^{-1}$.

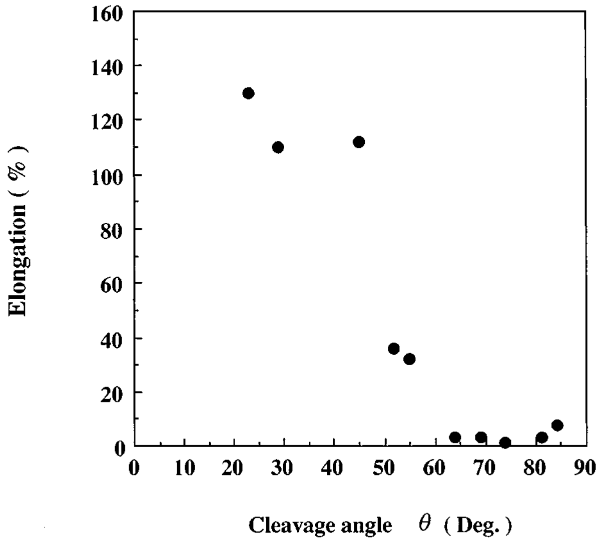

Figure 12 Elongation versus cleavage angle.

Single crystal zinc is known to exhibit similar behaviour. However, cleavage occurs with single bending only when the angle of the basal plane relative to the direction of applied stress becomes larger than 70° [8]. In this regard, the brittle range for bismuth crystal is much wider than that for zinc since bismuth shows brittle characteristics when the angle of the (111) plane with respect to the applied stress reaches ∼57°.

The practical ramification of this anisotropic behaviour of bismuth is that alloys containing bismuth are difficult to process to thin wire and sheet products from large starting ingots using rolling, drawing or extrusion processes if the bismuth phase exists as pure or nearly pure bismuth, or as the complex morphologies which are often observed in Sn-Bi, Pb-Bi, and In-Bi-Sn alloys [9, 10]. In this respect, the OCC process, which is a net-shape continuous casting process, can be used to advantage to produce wires and sheet products from these materials.

4. Summary

An experimental study was conducted in order to investigate the characteristics of bismuth wires produced by the OCC process. The results are summarized as follows:

1. Using the OCC process it was possible to produce bismuth single crystal wires ∼2 mm in diameter with casting speeds of 30, 100, and 170 mm min^{-1}.

2. Bismuth single crystal wires exhibited marked anisotropy during deformation due to differences in growth orientation.

3. At the faster casting speeds the growth orientation tended to be near the [111] direction.

4. Wires with cleavage angles greater than about 60° exhibited essentially zero ductility. On the other hand, wires with cleavage angle less than 50°, exhibited remarkable elongation behaviour, in excess of 100%.

Acknowledgements

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