Continuous Casting of Single Crystal Ingots by the O.C.C. Process

A. Ohno

JOURNAL OF METALS
A PUBLICATION OF THE METALLURGICAL SOCIETY OF AIME

Reprinted from JOURNAL OF METALS, Vol. 38 No. 1, January, 1986, p. 14-16.

Continuous Casting of Single Crystal Ingots by the O.C.C. Process

A. Ohno

To prevent the nucleation of crystals on the mold wall in the continuous casting of metals, a heated mold that maintained that temperature above the solidification temperature of the cast metal was used instead of the conventional cold mold. The cooling of the ingot was conducted outside of the mold. Heat was conducted axially along the ingot from the mold zone to the cooling zone.

The principle of the O.C.C. (Ohno Continuous Casting) Process® was applied to the horizontal casting and vertical (upward) casting of wire and plate-like ingots of Sn and Al. The ingots consisted of a completely unidirectionally solidified structure. It was possible to obtain a long single crystal ingot as a result of the growth competition of crystals.

INTRODUCTION

The growth of the electronics industry has steadily enabled the manufacture of smaller and more precise devices. This tendency makes it desirable to develop a process for producing an ingot which is free from even any grain boundary. Various processes are available for producing such material. According to the Bridman Process,[1] a metal is melted in a slender tubular vessel having a pointed lower end. The molten metal is gradually cooled at the lower end of the vessel. Another process[2] employs a vessel in the form of a slender groove with a constriction. A metal is melted in the vessel and is solidified unidirectionally through the constriction so that only a single crystal may grown. According to the Czochralski Process,[3] which is widely used for producing a single silicon crystal, a seed crystal is brought into contact with the molten metal surface, and withdrawn. None of these processes can, however, produce a long single crystal continuously because of the dimensional limitation of the apparatus or vessel available.

When a molten metal solidifies in a vessel, the crystals nucleated on the wall of the vessel and forming a stable solidified shell thereon, grow competitively. Also, the crystals with a direction of preferential growth closer to a direction of heat flow grow faster. This suggests that if a molten metal is cooled unidirectionally at one end of a slender vessel, and, if during its solidification it is possible to inhibit the growth of new crystals, the competition of growth of the crystals solidifying in the vessel may result in the formation of a single crystal. This occurs unless a plurality of crystals with a direction of preferential growth perpendicular to the cooling end of the vessel are nucleated.

Elimination of the nucleation source for new crystals during solidification permits a long single-crystal ingot to be continuously cast. The O.C.C. (Ohno Continuous Casting) Process[4] employs a mold which is heated to hold its inner wall surface at a temperature above the solidifying temperature of the molten metal to prevent the formation of new crystals on the wall surface of the mold. This is done while the ingot is cooled outside the mold, as shown in Figure 1. The ingot has a surface layer of molten metal when leaving the mold, which solidifies immediately after leaving the outlet. Even if many crystals may be nucleated at the end of a dummy, where the ingot begins to solidify, their growth competition eliminates all the crystals except one having a direction of preferential growth in the closest proximity to the casting direction. Consequently, a long single crystal is formed. This process can also continuously cast a long single crystal with desired crystal orientation by employing a seed crystal at the end of the dummy.

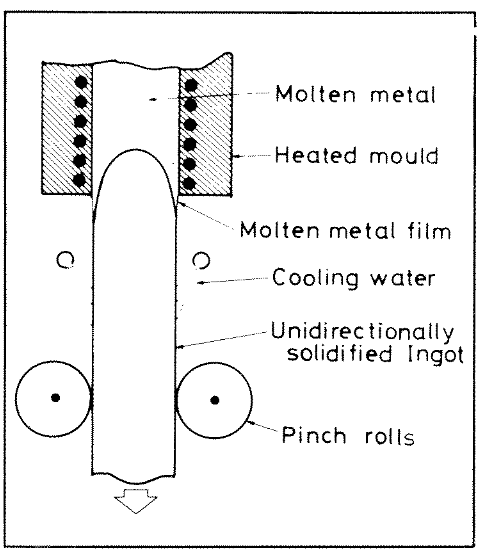


Figure 1. The principle of the O.C.C. Process.

RESULTS AND DISCUSSION

A 6 mm diameter wire of each of Sn and the Sn-Pb alloy and a 4 mm diameter Sn-Zn alloy wire were cast. If the mold temperature and the withdrawal speed were controlled to enable the surface layer of the casting to remain in a film of molten metal when leaving the exit end of the mold, both the Sn and the Sn-Pb alloy would form a 6 mm diameter single crystal wire at a distance of 500 to 1000 mm from the dummy end, irrespective of the solidifying conditions, even if no seed crystal was used.

A single crystal Sn wire with a diameter of 6 mm and a length of 10 m was produced using the aforementioned process. The 500 mm long portion of the wire from its leading end gave a tin cry upon bending and was found to be composed of a plurality of crystals. The remaining portion, however, did not give any tin cry, but was found to be composed of a single crystal. Figure 4 shows the Sn-30% Zn alloy wire produced at a casting speed of 800 mm/min. and having a diameter of 4 mm and a length of 50m. It was a wire composed of a single eutectic crystal free from any grain boundary, except the 300 mm long portion from its leading end.

The examination of the macrostructure of each of the 6 mm diameter Sn

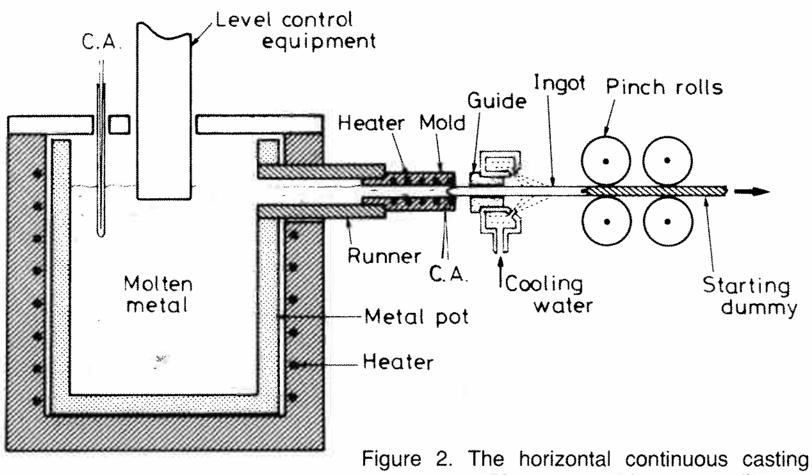


Figure 2. The horizontal continuous casting apparatus, 150 mm × 150 mm crucible.

EXPERIMENTAL CASTING TECHNIQUES

To cast a single-crystal ingot continuously in accordance with the principle described, it is necessary to reduce the pressure of the molten metal at the outlet end of the mold as far as possible to prevent it from flowing out. Two methods are practical for that purpose. One of them is a horizontal casting method employing a horizontal mold disposed in close proximity to the surface of the molten metal in a molten metal holding vessel. The other is an upward casting method which employs a vertical mold immersed in the molten metal and having an upper end at which an ingot begins to be formed upwardly.

The mold in Figure 2 was either a wire casting mold possessing a circular mold cavity with a 4 to 8 mm diameter or a plate casting mold having a 50 mm × 4 mm rectangular mold cavity. Each mold has a nichrome wire surrounding its cavity to heat the inner wall above the solidifying temperature of the molten metal. A horizontally movable water spray device was used for cooling the ingot.

A graphite guide protected the ingot against mechanical vibration. A level control bar of alumina was lowered into the molten metal to maintain a constant supply of the molten metal in the mold.

The experiments were conducted with 99.99% Sn, a Sn-5% Pb alloy, a Sn-38.1% Pb alloy, a Sn-30% Zn alloy, and 99.999% Al. Each of these metals and alloys was melted in the holding furnace. The continuous casting of 6 mm diameter 99.99% Sn and Sn-Pb alloy wires was tried first. The surface layer of the ingot was caused to solidify at a distance of less than about 2 mm outside the mold. Water was sprayed against the casting at a rate of 0.3 to 0.6 liter per minute at a distance 5 to 50 mm from the exit end of the mold.

Experiments were conducted by varying the temperature of the mold and the position of the cooling device at a wire withdrawal speed of 20 to 200 mm/min. A wire of the Sn-30%Zn alloy having a diameter of 4 mm was cast at a withdrawal speed of 800 mm/min. Wires of 99.999% Al having a diameter of 8 mm were cast at withdrawal speeds of 100 and 200 mm/min. Then, a Sn plate was cast using a graphite mold and aluminum dummy plate.

The experiments were conducted by using the upward continuous casting apparatus shown in Figure 3. It includes a graphite crucible disposed in an electric holding furnace and a mold formed from SiC and graphite. The mold has a nichrome wire surrounding its cavity and is covered with alumina cement to heat the inner wall immediately above the solvus. The mold is immersed in the molten metal and is vertically movable by a mold raising and lowering device so that its upper end may always stay at a level of height equal to the surface of the molten metal in the crucible. A graphite guide prevented swinging of the ingot during its upward withdrawal by pinch rolls.

The experiments were conducted with 99.999% Al, 99.9% Al and an Al-1% Si alloy. Each was melted in the crucible. A mold of SiC having a cavity diameter of 10 mm was immersed in the molten metal so that its upper end might be located at the same level of height as the molten metal surface. A dummy bar was brought into contact with the molten metal in the mold, and water was supplied to the cooling device for cooling the dummy bar. The dummy was gradually raised, and the mold lowered so that its upper end might always stay at the same level with the surface of the molten metal in the crucible. The surface layer of the ingot was caused to solidify immediately above the upper end of the mold. The casting of each metal or alloy was tried by varying the mold temperature, the position of the cooling device and the withdrawal speed.

Then, the continuous casting of a plate of each metal or alloy was tried by using a graphite mold having a 500 mm by 5 mm cavity.

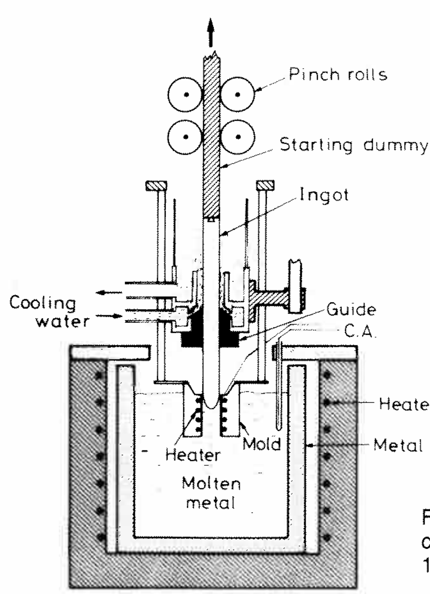


Figure 3. The upward continuous casting apparatus, 120 mm × 120 mm crucible.

and Sn-Pb alloy wires obtained at a casting speed of 20 to 100 mm/min. indicated that fewer crystals formed with the progress of the casting operation, eventually leaving a single crystal, unless the surface of the casting was scratched by the inner wall of the mold. Figure 5 shows the macrostructure of each of the Sn-38.1% Pb alloy ingots at the starting end of solidification and at a distance of 1000 mm. The macrostructure of cast eutectic alloy revealed a single eutectic crystal free from any grain boundary.

Striations were, however, often found on an ingot which macrographically appeared to be composed of a single crystal. The striations were more likely to form with an increase in the purity of Sn and with an increase in casting speed. Figure 6 shows the striations found on the surface of the 40 mm wide, 4 mm thick plate of 99.99% Sn which was cast at a speed of 60 mm/min.

Similar striations were found on ingots of high purity Al. Figures 6b and 6c show the striations found on the surfaces of 8 mm diameter ingots of 99.999% Al cast at a speed of 100 and 200 mm/min., respectively, and which were due to the growth of twin crystals.

The cross sectional macrostructure of each of the 10 mm diameter 99.9% Al and Al-Si alloy wires cast upwardly at various speeds and each having a mirror surface indicated that unless the surface of the casting was scratched by the inner wall of the mold, the polycrystaline structure would diminish with distance from the starting end of solidification, respective of the casting speed, as was the case with the Sn alloy casting produced by the horizontal method.

Figure 7 compares the macrostructure of the 50 mm wide, 5 mm thick plate of 99.9% Al cast by the upward casting method. With a 40 mm wide, 4 mm thick horizontally cast Sn plate. In both instances the casting speed was 40 mm/min. and a single crystal formed at a distance of 500 mm from the starting point of solidification in each case.

If the temperature of the inner wall surface of the mold is maintained at a level above the solidifying temperature of the molten metal, allowing the surface layer of an ingot to remain in a film of molten metal when leaving the mold, nucleation is inhibited on the inner wall surface of the mold. The number of crystals diminishes with the progress of the casting operation and eventually forms a single crystal irrespective of its purity.

This process is not only useful for the continuous casting of a long single crystal of a Sn or Al alloy, but also applicable to the production of a single crystal form, for example, Cu, Au, Ag, Fe or Ni if a mold made of an appropriate material is used, and if the atmosphere for the molten metal is appropriately controlled. The process will enable the continuous production of a single crystal having any desired cross section, such as a wire, plate or tube, if a mold having an appropriate cross sectional configuration is employed.

The continuous casting of a single crystal by this process will enable the crack-free production of a very fine electric wire with a smooth surface or a very thin metal foil. It will also enable the production of a single crystal from a difficult material, usually very susceptible to intergranular fracture.

Striations were often found on the ingots with an increase in casting speed. These striations appear to be due to the thermal strain resulting from fast solidification. Therefore, to continuously cast a material on which no such striation is desired, it will be necessary to select the casting conditions under which a flat boundary surface of solidification can be maintained.

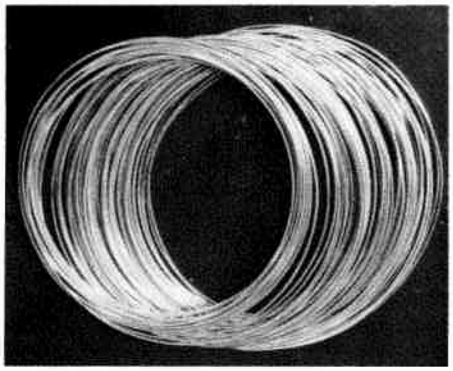


Figure 4. Sn-30 % Zn alloy single eutectic wire.

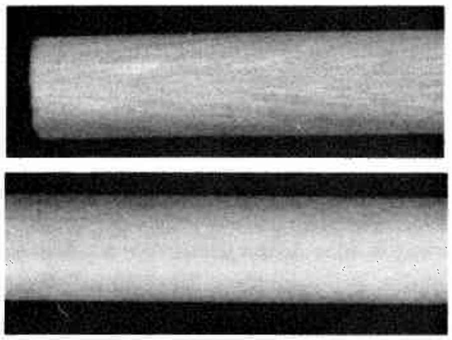
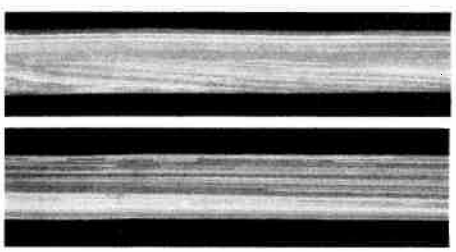


Figure 5. The macrostructure of Sn-38.1% Pb alloy wire. Top: starting end. Bottom 1 m from the starting end.

Figure 6a. Striations in a Sn plate; 60 mm/min.



Figures 6b and 6c. Striations in high purity Al ingots. (b) 100 mm/min. (c) 200 mm/min.

Figure 7a. The growth competition of crystals in a Sn plate.

Figure 7b. The growth competition of crystals in an Al plate.

References

1. B. Chalmers, *Principles of Solidification*, p. 301, John Wiley & Sons, Inc., New York, 1964.
2. J. Czochralski, *Z. Physik. Chem.*, 92, 219 (1917).
3. W.C. Winegard, *Introduction to the Solidification of Metals*, p. 87, The Institute of Metals, England, 1964.
4. A. Ohno, U.S.A. Patent 4,515,204; German Patent 3,246,470; Japanese Patent, 1,049,146; Canadian Patent 1,188,481.

ABOUT THE AUTHOR

A. Ohno is currently with the Chibat Institute of Technology of Narashino, Chiba-ken, Japan.