⁹ R. King, R. W. Cahn, and B. Chalmers: *Nature* (1948) **161**, p. 682; see also B. Chalmers: *Progress in Metal Physics*, pp. 127-162 (1949) New York. Interscience Publishers, Inc.

¹⁰ R. F. Miller: Influence of a Grain Boundary on the Deformation of a Single Crystal of Zinc. *Trans. AIME* (1934) **111**, pp. 146-157.

¹¹ W. Boas and M. E. Hargreaves: On the Inhomogeneity of Plastic Deformation in the Crystals of an Aggregate. *Proc. Royal Soc.* (1948) **193A**, p. 89.

¹² D. C. Jillson: An Experimental Survey of Deformation and Annealing Processes in Zinc. *Trans. AIME* (1950) **188**, pp. 1009-1018; *JOURNAL OF METALS* (August 1950).

Technical Note

Melting of Undoped Silicon Ingots

by J. Hino and H. E. Stauss

INTEREST in silicon has arisen again in the past decade as a result of improvements in crystal rectifiers.¹ Although the preparation of silicon was first reported by Berzelius in 1880, the early product was of relatively low purity, and only the need for rectifiers in World War II led to the production of a 99.9+ pct pure powder. This material in crystalline form was consolidated into massive silicon for use, and the method developed was to melt it with selected added constituents as "doping" agents. Melting techniques, therefore, are of great importance.

There are two basic problems in producing silicon ingots free of doping additions; one is the prevention of spitting and the other is prevention of cracking of the ingot during freezing. The most satisfactory arrangement yet developed for producing massive silicon is to melt and freeze in a cylindrical quartz crucible surrounded by a concentric heating element and concentric radiation shields or insulation. For example, use can be made of a tubular heater with a high frequency generator as the source of power and reflecting shields of alundum cylinders.

The spitting of silicon is related to gas evolution, and the gas comes from two primary causes—adsorbed gas and the reaction products of silicon and the crucible. Gas is also released from bubbles contained in the quartz crucible walls. Improved removal of adsorbed gas can be achieved by means of controlled melting and freezing. The seriousness of the problem in vacuo is reduced with an electrically operated mechanical movement of the high frequency power coil. The upper portion of the powder charge is melted first and the high frequency coil lowered until the powder is completely molten. During cooling the high frequency coil is raised slowly. These means also reduce the final nonviolent extrusion of large beads of metal through the ingot top during freezing. Better control of spitting and bead extrusion is obtained when melting is done under helium at atmospheric pressure instead of in vacuo.

The problem of reaction between silicon charge and crucible in practice is confined to the reaction between silicon and quartz. This² apparently is:

The part that this reaction plays in spitting has not been isolated for separate study. SiO is a volatile vapor at the melting point of silicon and is released freely during melting in vacuo, but hardly at all in helium at atmospheric pressure.

The cracking of ingots is a major difficulty in melting silicon, and its prevention requires special

melting techniques or the addition of "toughening" agents such as aluminum or beryllium.¹ The cracking of the ingots has been explained as being the result of the expansion that occurs upon freezing,³ although direct observation of freezing ingots reveals visible cracks on the surface only after a red heat has been reached, suggesting that cracking is the result of differential contraction of silicon and quartz. Silicon wets quartz, and the ingot adheres tightly to the crucible. Therefore as ingot and crucible cool, the two either have to pull apart, or at least one must crack. Surprisingly, in spite of the relative thinness of the quartz and the thickness of the ingot, the ingot and the crucible both crack. Microscopic and X-ray⁴ studies fail to show any plastic flow other than twinning in the ingots. Slow cooling fails to prevent cracking. Another possible solution to cracking is to weaken the crucible. Use of thin-walled crucibles finally led to success with fused quartz crucibles with a wall thickness of 0.25 to 0.50 mm. With such thin-walled fused quartz crucibles consistently uniform success is secured in producing sound ingots 30 mm in diam from the purest available grade of silicon (99.9+) without the use of any type of addition. Melts are made in the size range of 50 to 100 g.

Omission of a deliberately added doping agent is not sufficient to insure pure ingots. The reaction of silicon with crucibles and the resultant solution of impurities in the silicon is well-established.⁵ In this laboratory, the presence of Al, Be, and Zr has been found spectroscopically in ingots melted in contact with alumina, beryllia, and zircon. The best crucible materials reported in the literature are MgO and SiO₂. Use of MgO in this laboratory has resulted in a heavy deposit of magnesium on the furnace walls, showing that a reduction of the magnesia occurred and the resulting magnesium removed from the melt by volatilization. In the case of quartz, the silica is reduced and SiO liberated to deposit on the equipment walls. There probably is real danger that oxygen is dissolved in the ingot when either magnesia or silica is used as the crucible material. Preliminary analyses by Dean Walter in his vacuum unit in this laboratory⁶ indicate the presence of oxygen in undoped silicon melted in quartz.

References

¹ H. C. Torrey and C. A. Witmer: *Crystal Rectifiers*. (1948) New York. McGraw-Hill Book Co. This book contains full references to wartime reports.

² H. Dewet Erasmus and J. A. Persson: *Trans. Electrochem. Soc.* (1949) **95**, p. 316.

³ J. H. Scaff, H. C. Theuerer, and E. E. Schumacher: *Trans. AIME* (1949) **185**, p. 383; *JOURNAL OF METALS* (June 1949).

⁴ E. I. Salkovitz and F. W. von Batchelder: *JOURNAL OF METALS* (February 1952), *Trans. AIME*, p. 165.

⁵ F. Seitz: N.D.R.C. Report No. 14-110 (1942).

⁶ D. I. Walter: *Analytical Chemistry* (1950) **22**, p. 297.

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