Czokralski's Pulley

Jan Czokralski (1885-1953)

There's an old joke that you can spot crystallographers by their beards and their sandals. Beards are said to provide the rich source of heterogeneous nucleation necessary to grow the gem-like crystals that are a crystallographer's stock-in-trade. It's a reminder of just how weird the process of crystallization is, and the complexity that underpins an issue that is at once evocative and fundamental.
No-one who has tried to grow crystals in the lab can be unaware of the trade off between the twin processes of nucleation and crystal growth, words which conceal issues of ferocious complexity. Both began to be probed at the end 19^{th} century especially by the Estonian-German chemist and metallurgist Gustav Tamman. Tamman began to monitor the slow cooling of liquids in narrow test tubes to lay the groundwork for the understanding of crystal growth. Cooling the tubes he measured the rate at which the solid-liquid interface grew as a function of the degree of supercooling – the difference between the actual temperature of the liquid and the melting point. He proposed that crystallisation was a thermally activated process the rate of which was determined by the temperature at the solid/liquid interface. Although this idea was soon proven to be totally wrong, his many textbooks and monographs laid the foundation for much of the science that followed. His work on the kinetics of crystallization would be picked up by a young Polish chemist working in Germany.
Jan Czokralski was born the eighth, and youngest, son of a family of craftsmen in Exin (Ksynia) a provincial town in Poland. Growing up he developed a love of chemistry, conducting experiments, when he could, at home. When he finished school he apprenticed in a teacher training college but moved to Germany before qualifying. He then worked in a couple of pharmacies before starting a degree in chemistry at the Technical University in 1906. To make ends meet he worked for the duration of his studies, first in a chemical works and, from 1908, in the metals laboratory of the engineering firm AEG in Oberspree, then Germany's leading manufacturer of electrical cable. The lab had been set up by Wichard von Moellendorf, a young and enthusiastic engineer and metallurgist. Moellendorf conducted important studies into the plastic deformation of metals, experiments that questioned many of Tamman's ideas.
Although he finished his studies in chemical engineering in 1910, Czokralski never obtained a formal degree because his Polish school qualifications were never recognized. But with a full time job at AEG he began to conduct detailed crystallographic studies of metals. That he was no mere apprentice is indicated by the fact that in 1913 he succeeded Moellendorf as head of the lab. Although in a corporate environment, much of the work was fundamental, trying to understand the nature of crystallization and how to control it.
Legend has it that while waiting for a crucible of molten tin to solidify on his desk, Czokralski absent-mindedly dipped the nib of his pen into the metal rather than the ink-pot. As he withdrew his pen he drew a thin strand of metal several centimeters long. Czokralski immediately realized that he had found a new method to measure the rate of crystallization. Rather than follow the speed of the front, he would draw a filament out of the melt and measure the maximum rate above which the filament would snap. After a series of trials Czokralski found that the best method was to suspend a capillary by a silk thread above a crucible containing a metal only a few degrees above its melting point. The string ran over a pulley and then across to a motor whose speed could be adjusted. On lowering the capillary into the melt, the liquid would be drawn up the tube, and crystallize almost immediately, acting as a seed from which the filament could grow.
With this device Czokralski was able to make filaments over a meter long. Each was a single crystal. This represented a huge advance over the previous "Plitsch" method, which involved pressing metal powder with a binder into a rod. Heating the rod progressively along its length would recrystallize the grains into a single, crystalline rod. For metals like tungsten, Coolidge would show that careful swageing allowed the preparation of suitably ductile wire for the manufacture of incandescent bulbs (CK66, August 2013).
Czokralski's method did everything in one shot; as a result it had far more impact as a method of crystal growing than as a technique for studying crystallization rates. The availability of such perfect crystals of uniform width would play a crucial role in the study of plastic deformation and the discovery of the dislocations that make metals so shapeable. Already in 1922 Gompertz referred to "the Czokralski technique", and through the 20's and 30's paper after paper described variants of the method.
The technique would finally come into its own in 1948 when Gordon Teal at Bell Labs grew single crystals of germanium. Using a graphite crucible filled with the semiconductor heated to between 935-980 ˚C by an induction furnace, Teal introduced a seed crystal into the melt and very slowly pulled it upwards. At pulling at rates below 0.003 inches per second a cylindrical single crystal of unheard of levels of purity– a gleaming silvery "boule" of germanium – slowly emerged from the liquid. The crystals would allow Bell Labs to commercialise the first germanium-based "solid state" transistors.
But Teal, a native of Texas, was lured away by a competitor, Texas Instruments, for whom he developed a similar process to grow crystals of the much higher melting, but also more desirable element, silicon; its larger band gap promised significant advantages. At a conference in 1954 Teal ostentatiously showed off new silicon transistors, playing music by Artie Shaw on a gramophone record player. In contrast to their germanium counterparts, silicon transistor amplifiers kept the music playing even when dipped into a beaker of hot oil. The solid state revolution had arrived.
Today, the Czokralski method is used crystallize not just elements, but salts and oxides too, for optics, electronics and even jewellery. Today understanding nucleation remains one of the fundamental challenges of chemistry. And while we can understand why having a beard could help one as a crystallographer, the sandals remain a mystery, intractable to both computation and experiment.

Reference

J. Czochralski, Ein neues Verfahren zur Messung des Kristallisationsgeschwindigkeit der Metalle, *Z. Phys. Chem.*, **1918**, *92*, 219.