Zone Refining—William G. Pfann

Thirty-five years ago this July, Bell Labs researcher William G. Pfann first described the process of zone refining—a simple, elegant way to make materials very pure or having a desired level of impurities.

Zone refining and related techniques take advantage of the fact that impurities have different solubilities in the liquid and solid phases of a host material. Because it was first applied to making ingots of pure and doped semiconductors, zone refining and associated techniques paved the way for mass production and widespread use of transistors and the rapid development of the semiconductor industry.

The story of Pfann's discovery of zone refining is a fascinating study in creativity. He related the story in the *Bell Laboratories Record* in an article he wrote shortly before he died in October 1982.

Pfann began work at Bell Labs in 1935 as a messenger boy and took night classes in chemical engineering at the Cooper Union School of Engineering. By 1939 he was a laboratory assistant in a small group of physical metallurgists. One day, out of the blue, the head of the group, Earle Schumacher, said, "Bill, take half your time and do research on anything you want."

"It was hard for me to believe, but I got to it right away," Pfann recalled.

He grew some foot-long lead single crystals that he planned to deform so he could study slip bands created by the nonuniform nature of single crystal deformation.

Pfann wanted to add antimony but knew it would segregate and yield a nonuniform distribution if he used standard crystal freezing techniques. So he melted a short length of the lead ingot and added the antimony to the molten zone. Moving the furnace along the length of the crystal spread the antimony uniformly as the crystal froze again.

"It seemed like such an obvious idea to me that I was sure that everyone knew about it," Pfann said.

After World War II interrupted the semiconductor research, Bill Shockley, an inventor of the transistor, put intense pressure on the Bell Labs materials researchers to provide single crystals of germanium with unheard-of purity. Pfann recalled his 1939 idea, called zone leveling, and began to build a modified apparatus to try to purify the germanium. A molten zone moving through an ingot could do more than level out the impurities, he thought. It would remove them.

"Just then another colleague spoke to me about his idea for applying fractional crystallization to purify the germanium," Pfann wrote. He was going to "directionally freeze it," pour off the last 5 or 10% of the liquid, remelt, and repeat the process four or five times without removing the crucible from the furnace.

"I told him it sounded like a lot of work," said Pfann.

While leaning back in his chair with his head on his office window sill during his daily lunch hour catnap, the answer came to Pfann. Why not pass a long germanium ingot through a *series* of heating coils rather than just one?

"I remember the feet of the chair hitting the floor with a loud clack as I jumped up," Pfann recalled. "I ran next door and told a colleague about it. He thought it over for about five seconds and said, 'That's it! You've done it, Bill.' "

The process, called zone refining, worked spectacularly. "It converted the idea of repeated fractional crystallization from a cumbersome process to an extremeley simple one," he said. Each moving zone carried a fraction of the impurities to the ends of the ingot, leaving the center section purified. The final distribution of impurities depends on the size, number and direction of travel of the zones, the original distribution of impurities, and on the relative solubility of the impurities in the solid and molten states.

Variant zone melting techniques came rapidly: temperature-gradient zone melting, zone remelting, continuous zone refining, solid-vapor zone refining, and liquid-vapor zoning. A colleague of Pfann's conceived the "floating zone" technique for silicon, which could not be zone refined in a container.

Zone refining has been developed to where it can produce uniform crystal ingots with only one wrong atom in 10 billion—equivalent to a single grain of salt in a railroad carload of sugar.

Several years after his 1952 paper appeared, Pfann learned that Russian physicist Peter Kapitza had performed one-pass zone melting and described it in a 1928 paper.

"He was concerned with crystal growth and apparently did not recognize the potential of a molten zone as a distributor of solutes," Pfann wrote in a 1967 *Scientific American* article. "And it would seem that neither did any of the hundreds of physicists who must have read his paper."

"It is interesting to think that this whole chain of events began when an astute Bell Labs director trusted his instincts, and gave a young unlettered lab assistant time to do research on whatever he wanted," Pfann said.

Among his many honors, Pfann received the American Chemical Society's first Creative Invention Award in 1968. He reflected on the creative process in the *Record* article:

"The creative act is an ephemeral thing, which requires first of all hard work and total absorption in the subject," Pfann wrote. "Creativity also requires an uncanny ability to connect disparate ideas. I say uncanny because the process certainly does not appear logical. And I say ephemeral because there's just that fleeting moment, triggered by accident, in which the connection is made."

With catalysis by catnap, perhaps.

M.ROSS

Is there a topic you would like to read about in Historical Notes?

Send suggestions and comments to:

Editor, MRS BULLETIN
Materials Research Society
9800 McKnight Road, Suite 327
Pittsburgh, PA 15237
Telephone (412) 367-3036