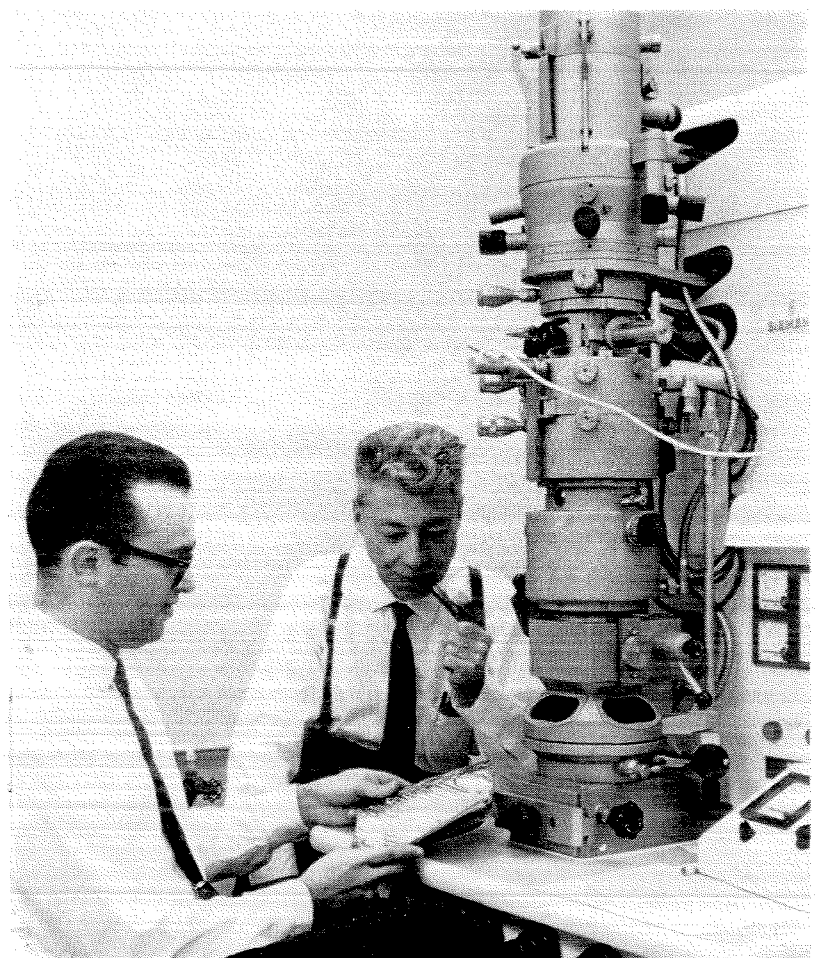
Rapid Cooling: A Way to Make Unusual Alloys

"Freezing" molten mixtures very fast can produce new materials with some unexpected properties



Ronald Willens and Pol Duwez use an electron microscope to check the structure of alloys made with the rapid cooling technique.

A new technique for metallurgical research, developed at Caltech, is producing some remarkable new alloys. By cooling molten material so fast that it doesn't have time to crystallize normally, Pol Duwez, professor of materials science, and Ronald Willens, assistant professor of materials science, can create thin foils of materials with some very unexpected properties.

The latest in a series of new alloys is a "metallic glass," composed of palladium and silicon. It doesn't have a crystal structure, but still has metallic properties. For example, this amorphous substance has electrical resistivity that is nearly constant over a temperature range from a fraction of a degree to about 375° K. Moreover, it can be made ferromagnetic with the addition of a small amount of iron, cobalt, or nickel. Crystalline alloys, too, that have been rapidly cooled often turn out to have properties markedly different from those they would have if cooled slowly. For example, a gold-germanium alloy obtained by rapid cooling is superconducting at 1.6° K, although neither constituent nor the alloy itself is superconducting normally. Another new alloy, a high-temperature phase of tungsten carbide, was found to be superconducting at 10° K, although it too would not normally be.

While it is true that amorphous alloys with metallic properties had been produced previously by vacuum deposition of the components on a target maintained at liquid helium temperature, they were stable only at quite low temperatures. The palladium-silicon glass is stable indefinitely at temperatures up to about 200°C. When heated, it changes to what is probably a transition crystalline phase at about 300°C.

Analysis of structure

That the alloy is truly amorphous has been shown with electron microscope photographs. The photographs, which have an effective resolution of about 30 angstroms for metallurgical work, do not show any discrete crystals; the interatomic distances involved in crystal formation make it unlikely that any could exist and not be seen. Also, electron and x-ray diffraction patterns confirm the electron microscope observations.

The amorphous palladium-silicon is perhaps an extreme example of the possibilities of rapid cooling; crystalline alloys with unusual structures are also of great interest. Moreover, they are much more likely to result from rapid cooling. Amorphous structures are generally the most unstable form and are much more difficult to produce. The crystalline alloys fall into two general classes. In one, the solubility of one metal in another can be greatly increased; in the other, new intermediate crystal phases, impossible to produce through normal equilibrium cooling techniques, can be made. Both may be quite stable at the relatively low level of room temperatures.

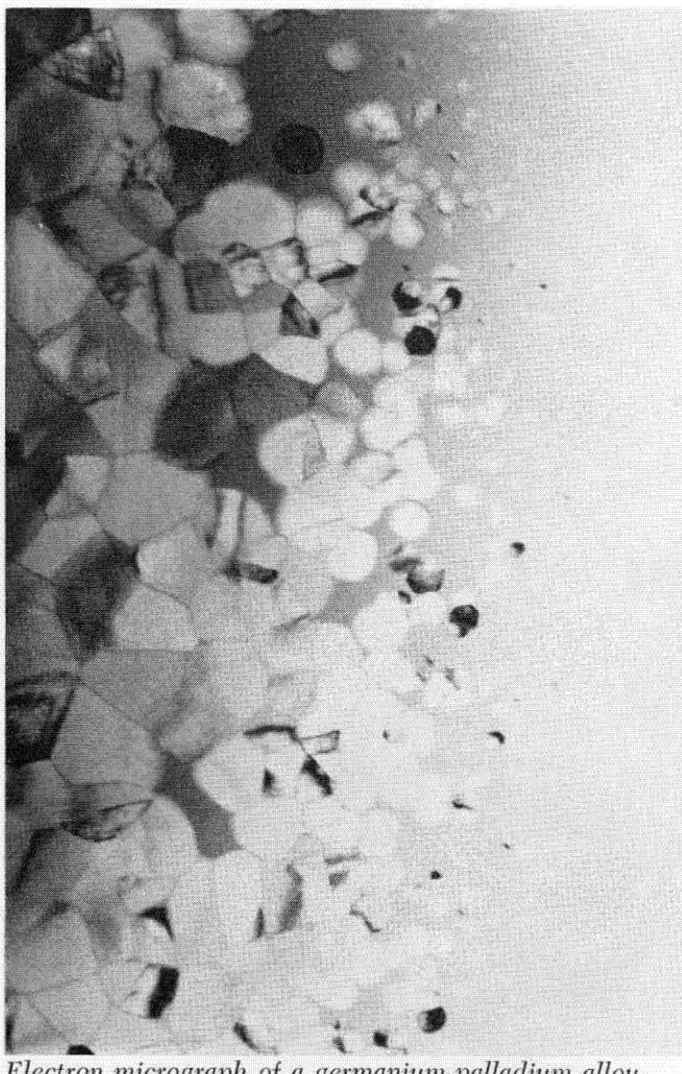
Rapid cooling technique

Two different techniques are being used for rapid cooling; they are dubbed the "gun" and the "piston and anvil" methods. The object is the same for both of them — to cool the molten material so quickly that the unoriented atoms in the liquid state are "frozen" in position, or are at least frozen into some unusual crystal structure. The method of cooling is to force the molten material to spread over a relatively cool surface very fast (on the order of a few thousandths of a second). The surface absorbs heat from the liquid, cooling it at a rate of more than several million degrees per second. However, because the liquid must be spread very thinly to achieve such high rates of cooling, the size of the foil that can be made with this process is limited.

The gun technique uses a shock tube to impart high velocity to a drop of molten material which is "shot" downward onto a curved copper strip. The drop impacts at a glancing angle, acquiring a radial acceleration that spreads it out on the copper. For lower quenching temperatures, the copper strip can be submerged in liquid nitrogen. The foil produced is about one centimeter wide and three or four centimeters long. Thickness may vary from about one-tenth to several microns. However, the thickness is not uniform, which limits the extent of tests that can be performed on the foil. Tests such as yield strength and tensile strength cannot be made.

The piston and anvil method does produce uniformly thick foils (about 45 microns thick). In this case the liquid is spread over two flat, heat-absorbing surfaces by the force of their impact, which occurs just as a drop falls between them. The action is initiated as the falling drop is sensed photoelectrically.

The range of possibilities of this technique is very broad. With the equipment now able to achieve temperatures of about 4000°C, rapid cooling of nearly any compound is possible. The work has been supported by the Atomic Energy Commission.



Electron micrograph of a germanium-palladium alloy, showing the transition from amorphous (right) to crystalline material. The left side is thicker, so it cooled more slowly and crystallized. Magnification: 54,000.