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HARDENED COPPER

This letter circular has been prepared to meet the frequent requests for information on the subject of "Hardened Copper".

The so-called "lost art" of hardening copper is no secret to present day metallurgists, and no reward for its discovery has been offered by the Government. Rumors to that effect have been circulated, and the National Bureau of Standards has received many inquiries concerning it, such requests for information being usually prompted by newspaper stories such as that of the "rediscovery" of the art by an automobile mechanic and its subsequent sale for a fabulous sum.

There is nothing new or "mysterious" in "hardened copper"; immense quantities are in commercial use and more is being added daily. Any well-informed metallurgist today knows how to produce an edged tool of hardened copper as good as any made in prehistoric times, but the knowledge is of no particular advantage to him because of the superiority of the steel tools now available. The result can be attained by any one of three well-known processes, or by a combination of them. Briefly, the three hardening processes depend upon (a) cold working, (b) alloying, and (c) heat treatment (after alloying).

Hardening (often referred to as "tempering") can be produced by cold rolling or hammering, cold-drawing, etc. Hard-drawn copper wire and cold-drawn tubing are examples. To supply the needs of a single industry alone, vast quantities of copper hardened by this means are used in hard drawn trolley wire. The presence of certain alloying elements in small percentages is usually desirable in such products.

The second method of hardening copper is to alloy it with a small amount of another metal or perhaps more than one metal. Zinc, tin, aluminum, and iron are the common additions. The alloyed metal, of course, cannot properly be referred to as "copper", but should be named according to the chief alloying constituent. Vast quantities of copper hardened in this general way are in commercial use. Many of the samples of "hardened copper" submitted to this Bureau for examination have been found to contain small amounts of one or more of the elements named above.

In one of the favorite methods of "hardening" copper, the melting apparently is manipulated (perhaps unwittingly on the part of the experimenter) so that the resulting melt is impregnated with oxide. Cuprous oxide is soluble in molten copper and in alloying with it behaves exactly like a metallic alloying element. Copper treated in this way is considerably harder and more brittle than the pure metal but is totally unsuited for most of the purposes for which copper is used.

The term "hardened copper" has been used above in its general sense to refer to copper in which the mechanical properties have been modified in the manner usually understood by the term "hardening", i.e., an increase in toughness, a decrease in ductility, etc. The popular conception of "hardened copper", however, is that of a metal similar to hardened steel and usually implies the "ability to take and carry a cutting edge".

Of the numerous samples of "hardened copper" submitted to this Bureau for examination, many were found to be impregnated with cuprous oxide, which indicates that alloying with oxide had occurred during the melting, as described above. Such a product is considerably harder and more brittle than pure copper and has a characteristic red color. Analysis of samples of "hardened copper" submitted by one inventor showed it to be simply aluminum bronze, an alloy well known for many years and used widely in industry at present. Several years ago a manufacturer of aluminum bronze distributed a small cold chisel of his material as an advertising novelty. This chisel would actually cut soft steel, though its edge was soon dulled. It was superior to the "hardened copper" axes of prehistoric times, however, and in those days would have constituted an important metallurgical advance. To the modern metallurgist, it is interesting but of no practical value.

One of the most widely used methods of measuring hardness is known as the Brinell method. A hardened steel ball is pressed into the metal and the diameter of the indentation is measured. The quotient of the load on the ball divided by the diameter of the indentation is known as the "Brinell hardness numeral". The higher this value the harder is the specimen. The following determinations of the Brinell hardness of different forms of copper and of a sample of so-called "hardened copper" submitted to the Bureau are of some significance:

Specimen	Bhn(500 kg load,10 mm ba
Hard-drawn trolley wire (23/64" diameter)	107
Hot-rolled; 1/4" sheet	68
Electrolytic (cathode) copper as deposited	59
"Hardened" copper, as submitted (sample contained 5.5 percent zinc)	39

Popular interest in the so-called "lost art" of hardening or "tempering" copper is also evidenced by the rather numerous patents covering such processes. The fantastic directions given in some of these patents are suggestive of medieval methods of working metals. The following is typical:

> "Heat the copper to 260° to 315° and subject it while hot to fumes of burnt sugar and animal fat at a temperature below that necessary to form carbon monoxide."

The search for new and better alloys of copper which may combine strength and resistance to corrosion, or strength and good electrical conductivity, is being unremittingly carried on by scientists. In ancient times weapons and cutting tools were sought; today the needs which the nonferrous metallurgist seeks to fill are, rather, those for materials more resistant to corrosion, as in the manufacture of chemicals or the carrying out of chemical processes; for strong, cheap and weather-resistant roofing materials; for better cables, trolley wires, and other electrical conductors; and for certain other specific uses.

Some of the copper alloys being studied by scientists with the idea of finding materials suitable for these modern purposes are decidedly harder than pure copper. Corson demonstrated ("Copper hardened by new method", Iron Age, 119, 424, 1927), also Bain ("Notes on the atomic behavior of hardenable copper alloys", Proc. Inst. Metals, Am. Inst. Mining and Metallurgical Engineers, 451, 1927) that various alloys of copper and silicon with a third metal such as nickel, chromium, or cobalt may be made strong and hard by heat treatment. The treatment consists in heating to such a temperature that the silicide which formed from the nickel and silicon goes into solid solution in the copper, quenching to retain the silicide in solution (after which the alloy is still soft), and then reheating or tempering to secure a controlled precipitation of the silicide. The precipitation of the fine particles of silicide hardens the alloy in a manner similar to the hardening of duralumin. This is the third method of hardening. But since several percent of alloying elements are needed to secure a marked ability to be hardened by quenching and tempering, such products are classed as alloys, not as "hardened copper" or "hardened aluminum".

The most important recent industrial development of this kind is the treatment of copper with a small percentage of beryllium. Beryllium alloys with copper in all proportions but the commercially useful alloys are limited, at the present time, to those containing about 0.7 to 2.5 percent of beryllium. In this range, the copper alloys (beryllium bronzes) are hardenable by the hardening treatment used for duralumin. The alloys are ductile and soft after being quenched in water from about 800°C and become hard only when heated subsequently to about 350°C. A tensile strength approaching 200,000 lb per square inch and a Brinell hardness number as high as 400 can be obtained. Many useful applications have been made of the beryllium-copper alloys, and their physical properties have been investigated in detail. A very promising application is for "non-sparking" tools, hammers, chisels, etc. used in explosive manufacturing plants, gasoline service stations, or wherever the fire hazard from explosive gas mixtures is to be guarded against at all times. Another use is as a spring material especially for elevated-temperature service.

Newspaper headlines usually refer to these newer alloys of copper as "hardened copper" and may imply that ancient secrets are being rediscovered. However, the metallurgists responsible for the developments would be the last to make such statements or to perpetuate the erroneous idea that these alloys can compete with modern tool steels for edged tools.

Relative to the so-called "lost art of hardening and tempering copper or bronze", the following quotation from Wm. Gowland (J. Inst. Metals, VII, 23, 1912) is of interest. Professor Gowland, formerly of the Royal School of Mines, London, was an authority upon the metallurgy of copper and especially its uses in antiquity.

> "The castings (knives, swords, etc.) generally are hammered at their cutting edges, and it is to this hammering and to it only, that the (increased) hardness of the cutting edges of both copper and bronze weapons is due, and not to any method of tempering. Much has been written about the so-called art of tempering bronze, supposed to have been practiced by the men of the Bronze Age in the manufacture of their weapons; the hardness is also said to be greater than can be given to bronze of the present day. I should like to correct this error, as it can only have arisen owing to its authors never having made any comparative practical tests of the hardness of bronze. Had they done so, they would have found that the ordinary bronze of today can be made as hard as any, in fact harder than most, of prehistoric times, by simple hammering alone."

It is, of course, not impossible that some of the ancient bronze implements may have owed part of their usefulness as weapons to the presence of certain impurities which served to harden the alloy and give it a fair cutting edge when heat treated in some fashion. Nickel is found in many of the ancient bronzes (Gowland, J. Inst. Metals, 7, 23, 1912; Chickashige, Trans. Chem. Soc., 117, 917, 1920), and silicon, though seldom reported in analysis of ancient copper alloys, might have been present in some. It appears most probable, however, that the hardening effect of tin which was often present, was the chief source of the hardness of the weapons, and it is unlikely that the superior hardness was obtained by quenching and tempering. It is much more probable that cold-working methods were employed.