A Historical Perspective on the Utilization of Phase Diagrams for Precipitation Hardening

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The suggestion in 1919 that precipitation would harden alloys had an immediate impact on the development of new alloys and led to a period of extremely active interest in careful phase diagram determinations. It also sparked a lively debate that had a lasting impact on physical metallurgy and led to a forerunner of dislocation theory.

In 1919, scientists of the U.S. Bureau of Standards (now the National Bureau of Standards) published two studies of aluminum age-hardening alloys. One was a set of phase diagrams. The other explored the consequences of various heat treatments on the subsequent time evolution of mechanical properties. The second study tentatively concluded that age hardening of aluminum was a room-temperature precipitation phenomenon and suggested that other alloys could be hardened by a thermal treatment that would lead to precipitation. Examination of phase diagrams would reveal which alloys were candidates for precipitation hardening and would provide both the solutionizing temperature and the range of temperature for the precipitation process.

This prescription proved to be astonishingly successful for developing new alloys. It led to a "golden age" of phase diagram determination that lasted two decades. It contributed to the development of a variety of fields in material science and launched a scholarly debate that overthrew old concepts and definitions concerning alloy phases.

The importance of the theoretical suggestion for the development of new alloys is clear from the record. At the end of the 19th century, cast iron was the only important commercial alloy not known to western technology at the time of the Romans. The accidental discovery of the age hardening of aluminum by Wilm occurred in 1904. This alloy quickly became an important commercial alloy, with the trade name Duralumin. In the fifteen-year interval between this discovery and the suggestion by the Bureau of Standards group, only one other age-hardening system had been discovered, but not published. Aging of Duralumin was thought to be a unique and curious phenomenon. By 1932, in his Institute of Metals lecture, Merica could tabulate experience with fourteen base metals (and Monel) which had all been discovered to precipitation harden, after 1919, in a total of more than one hundred different alloy combinations. Even this list was then incomplete and underestimated the true worldwide research effort that the theoretical suggestion had stimulated. Most of today's commercial alloys are precipitation hardened.

Merica could point with satisfaction to the far greater power of the metallurgist to improve the properties of metals by heat treatment as a result of the precipitation hypothesis. He noted, "Today, in consequence of our better understanding of the phenomenon generally known as age hardening, we are familiar with many alloys which are hardenable by heat treatment alone, including those of all the common ductile metals. In fact, it is possibly not an exaggeration to say, quite contrary to our older conception,
that hardenable alloys may be the rule rather than the exception among alloy systems."

Prior to 1919, hardenability of alloys through heat treatment had been associated only with phase changes such as those that occur in iron and its alloys. Merica wrote, "The few isolated cases which were known to harden by thermal treatment alone were deemed to be metallurgical gifts of good fortune." The use of the term "phase changes" was limited to situations in which a major phase disappears and one or more phases appears. Precipitation was not considered to be a phase change. It seemed that the aluminum phase diagram study had been motivated by the possibility of a phase change.

Almost twenty years passed before the precipitates responsible for the hardening were experimentally detected by a small-angle X-ray scattering. In the interim, the obvious success of the theory when applied was in sharp contrast with scholarly reservations. It became increasingly clear that precipitates conforming to the then-accepted definitions were not observed until long after hardening had begun. Often, hardening would peak before detectable precipitation, which would then be accompanied by softening. In response, Merica postulated the hardening agent to be clusters of solute atoms on atom sites in the original crystal, which distorted the crystal and made slip difficult. He called these clusters "knots". When they were finally detected, they became known as Guinier-Preston (GP) zones.

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Today, we believe them to be true precipitates of a metastable coherent phase obeying the laws of thermodynamic equilibrium, and they are often depicted as a metastable feature in phase diagrams.

The long resistance to this point of view is the result of old misconceptions and definitions concerning phases. Chemists long believed in the law of definite proportions and insisted on stoichiometry, homogeneity, and macroscopic size. The sought-for precipitates were expected to be compounds, to be distinct phases with their own crystal structure, and to be separated from the matrix by a sharply delineated interface. Long after GP zones had been detected, controversy about whether they were precipitates or pre-precipitates would rage.

The precipitation-hardening hypothesis stimulated a golden age of phase diagram determination. In the early part of this century, the concept of solid solubility had gradually become accepted as a general phenomenon. However, the temperature dependence of solubility limits was rarely investigated. Phase diagrams typically were shown with vertical solvus lines. Now, the temperature dependence of solid solubility acquired a scientific and practical importance. Accurate solubility data supplemented the earlier emphasis on phase transformation invariants and phase identification.

The precipitation-hardening hypothesis led to a number of insights into other phenomena. Jeffries and Archer concluded that the aluminum itself had to be inherently strong if such a small amount of precipitates could harden it. Their "slip interference theory" has been described as "the first theory of metal hardening to be based realistically on crystal structure and was the immediate precursor to dislocation theory." The entire episode is a wonderful example of the effect of a brilliant hypothesis on a field. Long before the hypothesis was proven, practical men were using it to develop new alloys, and scientists had reasons to study phase diagrams. Ultimately, the academic debate and the understanding it produced will have led to new endeavors whose scope was in no way predictable in 1919.

About the Authors of the 1919 Article

In 1919 Paul D. Merica, Romaine G. Waltenberg, and Howard Scott were employed by the U.S. Bureau of Standards in Washington, DC, in the laboratory on Connecticut Avenue pictured in Fig. 1 and 2. Merica and Scott had Ph.D.'s. Howard Scott was a local boy from Rockville, MD, who had begun as an 18-year-old apprentice in 1912. Even though he obtained an AB from George Washington University in 1918 and co-authored numerous papers, he remained an apprentice until he left the Bureau of Standards for Westinghouse Electric Company in 1925. He had a distinguished career at Westinghouse, becoming manager of the Metallurgy and Ceramics Department in 1946 and Chief Metallurgist in 1954. He retired in 1958. Romaine G. Waltenberg left the Bureau and continued active work on temperature control devices into the 1950's. After receiving his AB from DePauw University, Paul Merica taught chemistry in China before receiving his Ph.D. in Metallurgy and Physics from the University of Berlin in 1914. After five years at the Bureau of Standards he resigned, citing inadequate pay. In 1919 he joined the International Nickel Company, rising to become president and director from 1951 until his retirement in 1955. Both Scott and Merica received numerous honors; among them, the Hunt Award to Scott; and the Franklin Institute Medal, Douglas Medal, and Fritz Medal to Merica. In 1942, Merica became a member of the National Academy of Sciences which, after his death in 1957, published an extensive biography of him by Jeffries.