Precipitation Hardening of Metal Alloys

Precipitation hardening, or age hardening, provides one of the most widely used mechanisms for the strengthening of metal alloys. The fundamental understanding and basis for this technique was established in early work at the U. S. Bureau of Standards on an alloy known as Duralumin [1,2]. Duralumin is an aluminum alloy containing copper and magnesium with small amounts of iron and silicon. In an attempt to understand the dramatic strengthening of this alloy, Paul D. Merica and his coworkers studied both the effect of various heat treatments on the hardness of the alloy and the influence of chemical composition on the hardness. Among the most significant of their findings was the observation that the solubility of $CuAl_2$ in aluminum increased with increasing temperature. Although the specific phases responsible for the hardening turned out to be too small to be observed directly, optical examination of the microstructures provided an identification of several of the other phases that were present. The authors proceeded to develop an insightful explanation for the hardening behavior of Duralumin which rapidly became the model on which innumerable modern high-strength alloys have been developed.

In his Institute of Metals lecture [3], Merica summarized the Merica, Waltenberg, and Scott paper as follows: “The four principal features of the original Duralumin theory were these: (1) age-hardening is possible because of the solubility-temperature relation of the hardening constituent in aluminum, (2) the hardening constituent is $CuAl_2$, (3) hardening is caused by precipitation of the constituent in some form other than that of atomic dispersion, and probably in fine molecular, colloidal or crystalline form, and (4) the hardening effect of $CuAl_2$ in aluminum was deemed to be related to its particle size.”

At a symposium devoted to precipitation from solid solution, held nearly four decades after the original papers, R. F. Mehl noted [4], “The early work of Merica, Waltenberg, and Scott was the first contribution to theory: it demonstrated the necessity of a solid solubility decreasing with temperature; this paper had not only science but even prescience, for it suggested that some sort of precipitate-matrix interaction might contribute to hardening, long before coherency was even conceived. There are few better examples of the immense practical importance of the theory in the history of science; before Merica no new age-hardening alloys were discovered—the worker did not know where to look; following Merica, new age-hardening alloys came in a flood.”

The importance of the theoretical suggestion for the development of new alloys is clear from the historical record [5]. At the end of the 19th century, cast iron was the only important commercial alloy not already known to western technology at the time of the Romans. When age hardening of aluminum was discovered accidentally by Wilm [6], during the years 1903-1911, it quickly became an important commercial alloy under the trade name Duralumin.

The two NBS studies published in 1919 explored both the application of phase diagrams to the phenomenon and the consequences of various heat treatments on the subsequent time evolution of mechanical properties. The latter study tentatively concluded that age hardening of aluminum was a room-temperature precipitation phenomenon and suggested that it should be possible for other alloys to be hardened by a thermal treatment leading to precipitation. Merica et al. suggested that examination of the relevant phase diagrams would reveal which alloys were candidates for such precipitation hardening and would provide both the solutionizing temperature and the range of temperature needed 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 materials science and launched a scholarly debate that overthrew old concepts and definitions concerning alloy phases.

In the 15-year interval between the discovery by Wilm 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. However, by 1932, Merica could tabulate experience with fourteen base metals that had been discovered to harden by precipitation in a total of more than one hundred different alloy combinations. Even that list was already incomplete and underestimated the true worldwide effort that the theoretical suggestion had stimulated. Most of today’s high strength commercial aluminum and nickel-based alloys are precipitation hardened, as are many titanium and iron-based alloys.

Despite the practical success of the theory, there was skepticism since the precipitates did not grow to optically observable size until long after the hardening had begun. Almost 20 years passed before the precipitates responsible for the hardening were detected experimentally by small-angle x-ray scattering. When finally detected, they became known as Gunier-Preston (GP) zones. Today, they are regarded as true precipitates of a metastable coherent phase, obeying the laws of thermodynamic equilibrium, and are depicted as a metastable feature in phase diagrams.

The precipitation hardening hypothesis is now credited with insights into other phenomena, most particularly slip motions in crystals as presented in the slip interference theory [7]. The latter theory is acknowledged as the precursor to modern dislocation theory [8].

Fig. 1. Paul Merica, ca. 1932 (Reproduced with permission of the AIME).

Paul Dyer Merica had a rather remarkable career [9]. After attending DePauw University for three years, he went to the University of Wisconsin, earning an A. B degree in 1908. He then taught chemistry in China before receiving his Ph. D. in Metallurgy and Physics from the University of Berlin in 1914. He joined the U.S. Bureau of Standards that same year, holding the positions of research physicist, associate physicist, physicist, and metallurgist. In 1919 he joined the International Nickel Company, rising to become president and director from 1951 until his retirement in 1955. Throughout the course of his career, Merica received numerous awards, including the Franklin Institute Medal, the James Douglas Gold Medal, the Robert Franklin Mehl Award from the Minerals, Metals & Materials Society, the Fritz Medal, and, in 1942, he became a member of the National Academy of Sciences.

Prepared by Sam Coriell with reference to the historical account by John Cahn [5].

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